STUDIES ON COPPER(I)-SULPHUR INTERACTIONS AND CYANO-BRIDGED Cu(I)—CN—Ru(II) SYSTEM

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by
RAMSHARAN SINGH

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

JUNE, 1993

DEDICATED

to

MY PARENTS

STATEMENT

I hereby declare that the matter embodied in this thesis entitled **"STUDIES ON COPPER(I)-SULPHUR INTERACTIONS AND CYANO-BRIDGED Cu(I)—CN—Ru(II) SYSTEM"** is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology Kanpur, India, under the supervision of Professor S. K. Dikshit.

In keeping with the general practice of reporting scientific observations, due acknowledgment has been made wherever the work described is based on the finding of other investigators.

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CERTIFICATE I

It is certified that the work contained in this thesis entitled "STUDIES ON COPPER(I)-SULPHUR INTERACTIONS AND CYANO-BRIDGED Cu(I)—CN—Ru(II) SYSTEM", by Mr. Ramsharan Singh has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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CERTIFICATE II

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CHM 625	Principles of Physical Chemistry
CHM 632	Enzyme Reaction Mechanism and Enzyme Kinetics
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CHM 900	Ph.D. Thesis

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ACKNOWLEDGEMENTS

It is with great pleasure to express my deepest gratitude and sincere respect to Professor S. K. Dikshit for his inspiring guidance and patient supervision throughout the programme. His keen interest in my personal care and welfare is deeply acknowledged.

I feel extremely grateful to Mrs. Kamala Dikshit for her hospitality during my stay at I. I. T. Kanpur.

I am grateful to the faculty members of my department from whom I had privilege of learning different aspects. I wish to sincerely thank Professors B. D. Gupta, S. K. Dogra, U. C. Agrawal, T. K. Chandrashekar, V. Chandrashekar, N. Sathyamurthi, R. N. Mukherji, P. K. Bhardwaj and S. Sarkar for their help and encouragement.

I am extremely thankful to my seniors Dr. (Mrs.) Veena Singh (IIT Delhi) and Dr. H. K. Gupta (McMaster University, Canada) for their kind help which I gained in a short period of association during their stay in the lab. Thanks are also due to Dr. Rajendra Prasad (Vikram University, Ujjain), Dr. Surendra Prasad (Delhi Institute of Technology, Delhi) and Dr. D. S. Pandey (A. P. S. University, Rewa) for their help in many ways.

I feel pleasure to thank my friend Saifuddin Sheikh, for his cooperation, endurance, inspiration and support in odd circumstances throughout the programme. The cordial relations

with Sheikh will always be memorable to me.

I take privilege to thank Mr. Amit Sircar for his help right from my arrival in the Institute to the completion of the programme.

My gratitude is also due to Shri Nayab Ahmad for his keen interest in my research work and for recording many IR, NMR and electronic (UV-vis) spectra and elemental analysis of my samples.

I also wish to thank Shri Rajagopalan for recording some of the IR spectra of my samples. The instrumental facilities extended by RSIC CDRI Lucknow for the CHN analysis and recording ^{13}C and ^{31}P NMR spectra are also acknowledged.

I express my thanks to Shri B. N. Shukla for his technical help at all times, and messrs M. L. Sharma, D. K. Kanaujia, K. K. Bajpai, R. D. Singh, Anil Jauhari, Banwari Lal, U. S. Mishra, L. P. Tripathi, S. B. Chaghtai, V. N. Katiyar and Smt. S. Pathak for their kind help.

I also wish to thank Bhishma Kr. Patel, Manbendra Ray, S. Mandal, Tapan Lal, Vandana Dixit, Mani Oberoi, Pramod Kumar, Sanjay Kumar, K. R. Justin Thomas, Kalyan Raman, K. Raghunathan, Ravi Kant, Samar Kr. Das, Imanual, Drs. Ranjit Sarpal, Shalini Nigam and Damodar Reddy for their help.

Last but not the least, I record my profound sense of gratitude to my parents and other family members for their sacrifice in various ways for my endeavour.

Ramsharan Singh

SYNOPSIS

A considerable amount of work has been done to explore the coordination properties of thione donor ligands towards copper(I). These studies have been stimulated by a desire to understand more clearly the electronic and steric factors which influence the stoichiometry, geometry and reactivity of copper(I) complexes with thione ligands. Recently, the synthesis of mixed ligand complexes of copper(I) with thione ligands and triphenylphosphine, -arsine, -stibine etc have been reported and the steric factors discussed. In most of the cases halides, pseudohalides, nitrates and sulfates remain as a part of the coordination sphere. In contrast, the thione ligands react with $[Cu(CH_3CN)_4]^+$ to give luminescent tetrameric and hexameric complexes of copper(I). The thione ligands are deprotonated in these tetra- and hexanuclear complexes. It is interesting to note that these ligands react with $[Cu(PPh_3)_4]^+$ to give disubstituted compounds $[Cu(PPh_3)_2(thione)_2]^+$ and there is no deprotonation of the thiones. In addition, research activity has been initiated in

this field because of biological importance of copper and the photophysical properties of copper(I) complexes with 2,2′-bipyridine, 1,10-phenanthroline and their substituted derivatives. In view of the diverse and intriguing nature of copper(I)-sulphur interaction, we were also prompted to study the ligating behaviour of thiones towards copper(I).

The photophysical properties of the Ru(II) complexes are known for a long time and recently the nucleophilic character of the nitrogen atom in M—CN group has been exploited to synthesize a number of homo- and heteronuclear cyano-bridged complexes. In order to provide more information on such interesting compounds we have attempted to prepare and characterize hitherto unknown Cu(I)—CN—Ru(II) complexes. Our prime aim is to elucidate the change in ν(CN) when it is bridged between two electron rich centres namely copper(I) and ruthenium(II). The study of photophysical properties of these novel systems should be of considerable interest.

The thesis is divided into seven chapters. The first chapter describes the scope and the purpose of the study and gives a brief review of the relevant literature covering the synthesis, reactivity and spectral [electronic (UV-vis), IR and NMR] properties of various starting complexes and ligands related to the work described in this thesis. A brief survey of the literature regarding thiolate complexes of copper(I)

has also been made.

In chapter two, the reactions of 3-phenyl-2-thioxo-imidazolidin-4-one (ptiH), 5-mercapto-1-phenyl-1,2,3,4-tetrazole (mptH) and 1-morpholinoformanilide (mtfH) with the complexes $[Cu(PPh_3)_3X]$ (X = Cl, Br, I) have been described. These reactions yield the products $[Cu(PPh_3)_2(LH)X]$ (LH = ptiH, mptH, mtfH). All the products have been characterized by elemental analyses, electronic(UV-vis), IR, and ^1H NMR spectral studies, magnetic and conductivity measurements. The coordination site, namely thione sulphur has been decided on the basis of IR spectroscopy. The ligands remain in the thione form as indicated by the presence of ν(NH) and absence of ν(SH).

In chapter three triphenylarsine analogues of $[Cu(PPh_3)_2(LH)X]$ (LH = ptiH, mptH) complexes, have been reported and characterized.

Chapter four describes the reactions of the ligands dmptH, dbptH and tzdtH with $[Cu(PPh_3)_3X]$. The products $[Cu(PPh_3)_2(LH)X]$ have distorted tetrahedral environment around copper(I). The IR, ^{13}C and ^{31}P NMR data support the proposed structure.

In chapter five the synthesis and characterization of triphenylarsine analogues of $[Cu(PPh_3)_2(LH)X]$ are described.

The chapter six describes the synthesis, character-

ization and spectral studies of cyano-bridged copper(I)-ruthenium(II) complexes. It is observed that the reaction between PPh_3 and CuCN gives the tricoordinate compound $[Cu(PPh_3)_2CN]$ and not $[Cu(PPh_3)_3CN]$ unlike $[Cu(PPh_3)_3X]$. Reactions of L—L (L—L = 2,2′-bipyridine, (bpy); 1,10-phenanthroline, (phen)) with $[Cu(PPh_3)_2CN]$ give the tetracoordinate compounds $[(L—L)Cu(PPh_3)CN]$ by elimination of one phosphine. This reaction is very similar to the reaction of L—L on $[Cu(PPh_3)_3X]$ which yields $[(L—L)Cu(PPh_3)X]$ by elimination of two phosphines. The copper(I) centre of the complexes $[(L—L)Cu(PPh_3)CN]$ is electron rich, and the CN of the Cu—CN group has nucleophilic character. Ruthenium(II) centre is electron rich in $[Ru(bpy)_2Cl_2]$ and $[(\eta^5\text{-}Cp)Ru(PPh_3)_2Cl]$ and Cl group is labile. The nucleophilicity of CN in Cu—CN group and the lability of Cl in Ru—Cl bond have been exploited to synthesize the following cyano-bridged complexes: $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$, $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$, $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]BF_4$, $[(L—L)(PPh_3)Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$, and $[(L—L)(PPh_3)Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$. The spectral studies support the formation of Cu(I)—CN—Ru(II) group in these complexes. The remarkable feature of these complexes is the shifting of ν(CN) to the lower region, which is not very common. This is assigned to excessive back bonding because

- is bridged between two electron rich centres. According
› the literature reports $[Cu(L—L)_2]^+$, $[Cu(PPh_3)_2(L—L)]^+$,
₹u(bpy)$_2$Cl$_2$] and the homo- and heterometallic cyano-bridged
ıthenium(II) complexes show remarkable photophysical
roperties. It is expected that the cyano-bridged complexes
ynthesized by us, may also exhibit photophysical properties.
he studies on photophysical and electrochemical (CV)
›roperties of these complexes are in progress.

CONTENTS

LIST OF ABBREVIATIONS

Ar	phenyl—, *m*—, *o*—, *p*—tolyl
$AsPh_3$	triphenylarsine
biq	2,2'—biquinoline
bpy	2,2'—bipyridine
bpym	2,2'—bipyrimidine
$bzimtH_2$	benzimidazoline—2—thione
bzoxtH	benz—1,3—oxazoline—2—thione
bztztH	benz—1,3—thiazoline—2—thione
Cp	cyclopentadienyl anion
CT	charge transfer
CV	cyclic voltammogram
cyclam	1,4,8,11—tetraazacyclotetradecane
dbptH	N,N—dibutyl—N'—phenylthiourea
dcbpy	4,4'—dicarboxy—2,2'—bipyridine
dien	diethylenetriamine
dmeimdt	N,N'—dimethyl—1,3—imidazolidine—2—thione
dmeimt	1,3—dimethylimidazole—2—thione
dmgH	dimethylglyoxime

dmphen	2,9—dimethyl—1,10—phenanthroline
dmptH	N,N—dimethyl—N'—phenylthiourea
2,3—dpp	2,3—bis(2—pyridyl)pyrazine
2,5—dpp	2,5—bis(2—pyridyl)pyrazine
dppe	$Ph_2CH_2CH_2PPh_2$
dppm	$Ph_2PCH_2PPh_2$
dtu	dithiouracil
en	ethylenediamine
ESA	excited state absorption
ET	reverse-electron-transfer
etimdtH	N—ethyl—1,3—imidazolidine—2—thione
HEDTA	N—hydroxyethylethylenediaminetriacetate
HOMO	highest occupied molecular orbital
$imdtH_2$	1,3—imidazolidine—2—thione
$imtH_2$	imidazole—2—thione
IT	intervalence transfer
LF	ligand field
LMCT	ligand to metal charge transfer
$mebzimtH_2$	5—methyl—2—benz—1,3—imidazoline—2—thione
meimdtH	N—methyl—1,3—imidazolidine—2—thione
meimtH	1—methyl—1,3—imidazoline—2—thione
Me(OH)pymtH	4—hydroxy—6—methylpyrimidine—2—thione
MLCT	metal to ligand charge transfer
MMCT	metal to metal charge transfer

mptH	5—mercapto—1—phenyl—1,2,3,4—tetrazole
m—T	*meta*—tolyl
mtc	di—*n*—propylmonothiocarbamate
mtfH	1—morpholinoformanilide
NBETA	N—benzylethylenediaminetriacetate
$nbzimtH_2$	5—nitro—2—benz—1,3—imidazoline—2—thione
o—T	*ortho*—tolyl
oxt	1,3—oxazolidine—2—thione
Pcy_3	tricyclohexylphosphine
phen	1,10—phenanthroline
pip	piperidine
pit	pyrrolidine—2—thione
PPh_3	triphenylphosphine
p—T	*para*—tolyl
PTC	phenylthiocarbamyl
ptiH	3—phenyl—2—thioxoimidazolidine—4—one
pur6SH	purine—6—thione
py—3—Cl	3—chloropyridine
py—4—NH_2	4—aminopyridine
pymtH	pyrimidine—2—thione
$py1S^-$	mono deprotonated 1*H*—pyridine—2—thione
py2SH	1*H*—pyridine—2—thione
py4SH	1*H*—pyridine—4—thione
$qnotH_2$	quinazolinone—2—thione

qn2SH	quinoline—2—thione
RR	Resonance Raman
^{-}SPh	thiophenoxide
$^{-}S_2C$—*o*—T	dithio—*o*—toluate anion
$^{-}S_2C$—*p*—T	*p*—tolyldithiocarboxylate
tclH	ω—thiocaprolactam, hexamethylene—imine—2—thione
totp	tri—*o*—tolylphosphine
tptp	tri—*p*—tolylphosphine
tu	thiourea
$tzdt^{-}$	mono deprotonated 1,3—thiazolidine—2—thione
tzdtH	1,3—thiazolidine—2—thione

CHAPTER 1
INTRODUCTION

1.1 SCOPE AND PURPOSE

Currently copper(I) coordination chemistry is receiving much attention in an attempt to unravel the role of metals in biological systems[1-4] and the photophysical properties[5-15] of copper(I) complexes. The copper sulphur interactions in biological systems *e.g.* in plastocyanin,[1] "blue" copper proteins[16] and in thionein protein[17] are known since long time. The great interest in copper(I) complexes stems in part from the unique and sometimes puzzling variation in their structural formats[18,19] and chemical reactivity with the changes in ligands. The recent findings[20-24] that copper(I) can form high nuclearity complexes have added an additional and intriguing dimension to copper(I) chemistry. The size of the copper cores ranges from two to twelve[20-24]. However, copper(I) complexes of high nuclearity are still sparse and the number of examples sharply decreases with the increasing

nuclearity. Moreover, copper(I) can adopt mono-, di-[25], tri-[26-28], tetra-[29] and penta-[30,31] coordination sphere around it, which basically depends upon the bulk as well as the electronic properties of the ligands. In the past few decades the coordination properties of the ligands containing secondary thioamide (H—N—C=S) groups have been extensively investigated.[32] In the biological systems, these ligands play significant role in view of their pharmacological,[33-35] antiviral and anticancer activities.[36-37] Enormous amount of work has been carried out to understand these biological processes. A number of copper(I) complexes of the ligands containing H—N—C=S group and mixed ligands complexes containing -phosphines and -arsines are reported and many of them have been structurally characterized. Most of them have tetrahedral environments. Recently the photophysical properties of the tetra and hexanuclear copper(I) complexes of deprotonated thione (N—C—S)$^-$ have been reported. Moreover, the photophysical properties of copper(I) complexes of 2,2′-bipyridine, 1,10-phenanthroline and their analogues have been extensively studied. The aim of the work described in the thesis is to further our knowledge in the field of copper-sulphur interactions.

The photophysical properties of the ruthenium polypyridine complexes have been thoroughly

investigated.[38-50] These complexes range from mononuclear[38] complexes $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2X_2]$ (X = Cl, Br, I, CN) etc. to the recently developed polynuclear complexes of high nuclearity.[39-50] In the synthesis of the high nuclearity polypyridine complexes *e.g.* hexanuclear[43] complex $\{[(bpy)_2Ru(BL_a)]_2Ru(BL_b)Ru[(BL_a)Ru(bpy)_2]_2\}(PF_6)_{12}$, ($BL_a$ = BL_b = 2,3-dpp, 2,5-dpp) (2,3-dpp = 2,3-bis(2-pyridyl)pyrazine, 2,5-dpp = 2,5-bis(2-pyridyl)pyrazine), heptanuclear[41] complex $Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3^{14+}$, decanuclear[44] complex $[Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_2\}_3]^{20+}$ (biq = 2,2′-biquinoline) and tridecanuclear[47] complex $Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3^{26+}$ etc., the bridging ligands are chosen from the tetradentate polypyridines. In such a process the strategies of "Complexes as Metals and Complexes as Ligands"[44] have been used in which one unit, called building block, acts as a "Metal Center"/"Ligand System" for the other unit and vice versa.

The cyano-bridged homodinuclear complexes *e.g.* $[(NH_3)_5Ru(\mu\text{-NC})Ru(bpy)_2CN]^{3+}$ [51], $[(NH_3)_5Ru(\mu\text{-NC})Ru(bpy)_2(\mu\text{-CN})Ru(NH_3)_5]^{6+}$ [51], $[(CO)_3(bpy)Re(\mu\text{-CN})Re(bpy)(CO)_3]^{+}$ [52], $[(H_2O)(bpy)_2Ru(\mu\text{-NC})Ru(dcbpy)_2(\mu\text{-CN})Ru(bpy)_2(H_2O)]$[53] (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) etc. and heterodinuclear complexes *e.g.* $[(NC)(bpy)_2Ru(\mu\text{-CN})Pt(dien)]^{2+}$ [54] (dien = diethylenetriamine), $[(CO)_3(bpy)Re(\mu\text{-NC})Ru(bpy)_2(\mu\text{-CN})Re(bpy)(CO)_3]^{2+}$ [52],

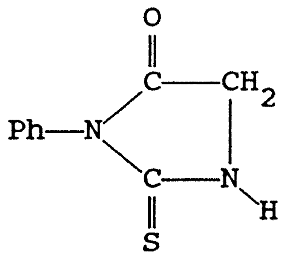
$[Cl(bpy)_2Os^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^{3+}$,[55] and $[(bpy)_2Os^{II}\{(\mu\text{-}CN)\text{-}Ru^{III}(NH_3)_5\}_2]^{6+}$[55] etc., have been reported. Detailed information about the stretching frequency of the bridged and terminal cyanide group and the photophysical properties of such complexes are available. Hitherto unknown, copper(I)-ruthenium(II) cyano-bridged complexes are described in this thesis. Both copper(I) and ruthenium(II) are the electron rich centres in their complexes with π-acid ligands and have shown remarkable photophysical properties. The nucleophilic property of the cyanide group in M—CN unit in $[Cu(PPh_3)_2CN]$, $[(bpy)Cu(PPh_3)CN]$, $[(phen)Cu(PPh_3)CN]$ and the labile nature of the chloride groups in $[Ru(bpy)_2Cl_2]$ and $[(\eta^5\text{-}Cp)Ru(PPh_3)_2Cl]$ complexes, have been exploited to synthesize the cyano-bridged complexes.[56,57] These properties have been utilized to synthesize cyano-bridged copper(I)–ruthenium(II) complexes where cyanide is bridged between two highly electron rich centres. The aim of our study is four-fold:

1. Thiones as ligands are potentially ambidentate or multifunctional donors and also exhibit thione-thiol equilibrium. Hence it is worthwhile to study variety of coordination modes of the thione ligands towards copper(I) metal centre.
2. To study the nature of Cu(I)—S, Cu(I)—P and Cu(I)—As

bonding in the mixed ligand complex systems.

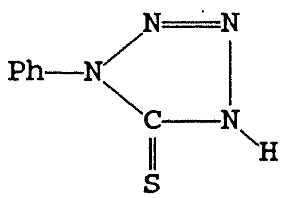
3. To study the reaction between [$Cu(PPh_3)_2CN$] and 2,2′-bipyridine, 1,10-phenanthroline.
4. To study the reaction between copper(I) mixed cyanide complexes and ruthenium(II) chloro complexes with π-acid ligands followed by the investigation of the spectral properties of the cyano-bridged copper(I)-Ruthenium(II) complexes thus obtained and effect of two electron rich centres on ν(CN).

The thione ligands chosen for these studies are as follows.



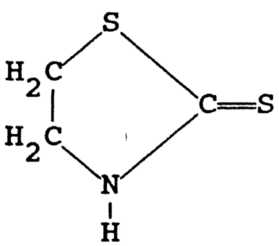
3-phenyl-2-thioxoimidazolidine-4-one

(ptiH) (I)



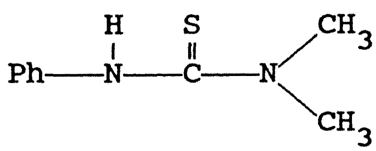
5-mercapto-1-phenyl-1,2,3,4-tetrazole

(mptH) (II)



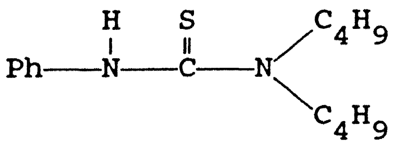
1,3-thiazolidine-2-thione

(tzdtH) (III)

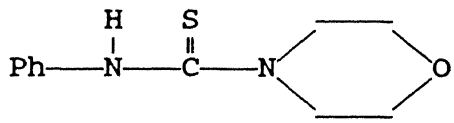


N,N-dimethyl-N′-phenylthiourea

(dmptH) (IV)



N,N-dibutyl-N′-phenylthiourea (dbptH) (V)



1-morpholinoformanilide (mtfH) (VI)

1.2 BRIEF REVIEW

The syntheses, reactivities, structural and spectral aspects of the precursor complexes and ligands utilized in the preparation of new compounds reported in this thesis are briefly reviewed in the following sections. This has been done to incorporate some modifications that have been introduced in the present work.

1.2.1 $[Cu(EPh_3)_3X]$ (E = P, As) (X = Cl, Br, I)

1.2.1(a) Synthesis and Reactivity

$[Cu(PPh_3)_3X]$ (X = Br, I) was first prepared by Costa et al[58] by the reaction between the copper salts and CH_3MgX (X = Br, I) in the presence of PPh_3. But, later on they prepared[59] the complex by the direct reaction of cuprous salt CuX (X = Cl, Br, I) and excess triphenylphosphine in benzene or chloroform. In the same year Cariati and Naldini[60] described the preparation of $[Cu(PPh_3)_3Cl]$. In 1968, Lipard and Ucko[61]

reported the preparation of these complexes according to almost similar procedure. Later on Jardine et al[62] reported a new method of preparation of $[Cu(PPh_3)_3X]$ by using triphenylphosphine as reducing agent in which they refluxed 3.5 equivalent of triphenylphosphine with 1 equivalent of copper(II) halide in ethanol. The methods of Costa et al[59] and Jardine et al[62] are quite convenient to get reasonably pure compounds in good yield.

The important feature of the chemistry of $[Cu(EPh_3)_3X]$ is the facile replacement of one or two phosphine/arsine groups by the neutral ligands,[62] and that of halides by mono anionic ligands.[63,64] A number of copper(I) complexes of triarylphosphine and triarylarsine complexes having heterocyclic thione donor ligands have been reported[29,65-75] which are either synthesized by the reaction of $[Cu(EPh_3)_3X]$ and the thione ligands or by the reaction of copper(I) halide with thione ligands and triphenylphosphine or arsine.

1.2.1(b) IR Spectra

IR spectra of $[Cu(PPh_3)_3Cl]$ and $[Cu(AsPh_3)_3Cl]$ are shown in Figure 1.1. All the vibrations are mainly due to the phenyl groups of the PPh_3 or $AsPh_3$ ligands.[59] The characteristic bands of PPh_3 and $AsPh_3$ ligands are 1088 and 1075 cm^{-1} respectively.[76]

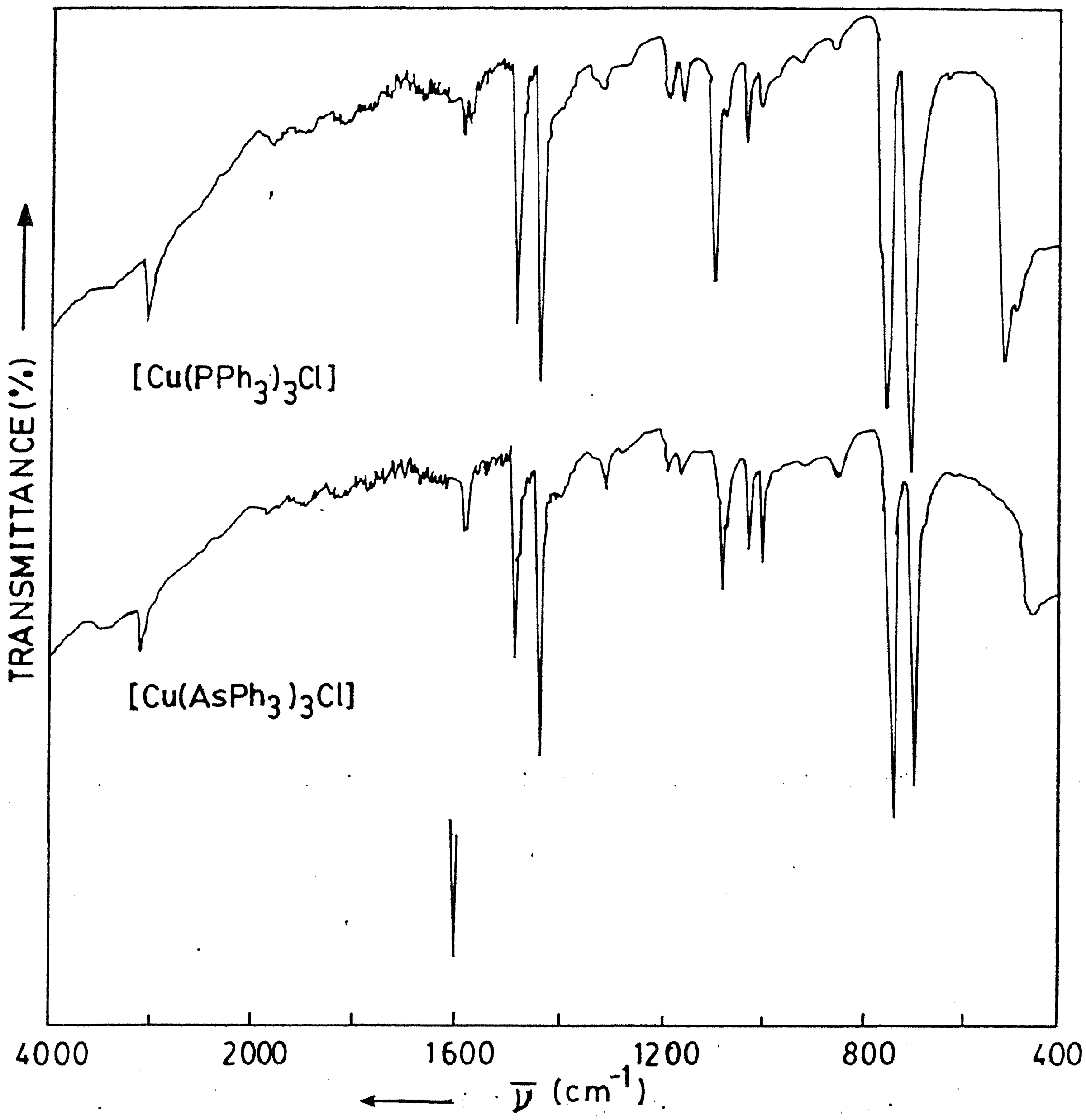


Figure 1.1. The IR spectra of the complexes [Cu(PPh$_3$)$_3$Cl] and [Cu(AsPh$_3$)$_3$Cl].

1.2.1(c) ^{1}H, ^{13}C and ^{31}P NMR Spectra

The ^{1}H NMR spectra of $[Cu(EPh_3)_3X]$ in $CDCl_3$ show the multiplets in the range 7.0-8.0 ppm(δ) due to the aromatic protons of the phenyl groups. The ^{13}C NMR spectrum[77,78] of PPh_3 shown in Figure 1.2, gives the peaks at 137.2 (doublet), 133.6 (doublet), 128.2 (doublet) and 128.5 (singlet) ppm(δ) for the P—C, *ortho-*, *meta-* and *para-* carbon atoms respectively. The ^{31}P NMR spectrum of PPh_3 provides only one signal at -6.0 ppm(δ) with reference to 85% H_3PO_4 (external reference).[78]

1.2.1(d) Electronic (UV-vis) Spectra

The typical electronic spectra[5,79] of PPh_3 and $[Cu(PPh_3)_3Cl]$ are shown in Figure 1.3. Triphenylphosphine molecules exhibit an intense UV absorption band arising from $l \longrightarrow a_\pi$ transition. This type of transition involves the promotion of an electron from the lone pair orbital (l) on phosphorus to an empty antibonding orbital of π origin (a_π) situated on a phenyl ring, Figure 1.4. Upon coordination of the phosphine molecule, the electron pair that formerly resided in the l orbital now engages in σ bonding to the metal atom. Accordingly, the transfer of an electron from this σ-orbital to the a_π orbital of the phenyl ring has been designated as a $\sigma \longrightarrow a_\pi$ transition, Figure 1.4. Since the π system of the phosphine ligand may interact with metal

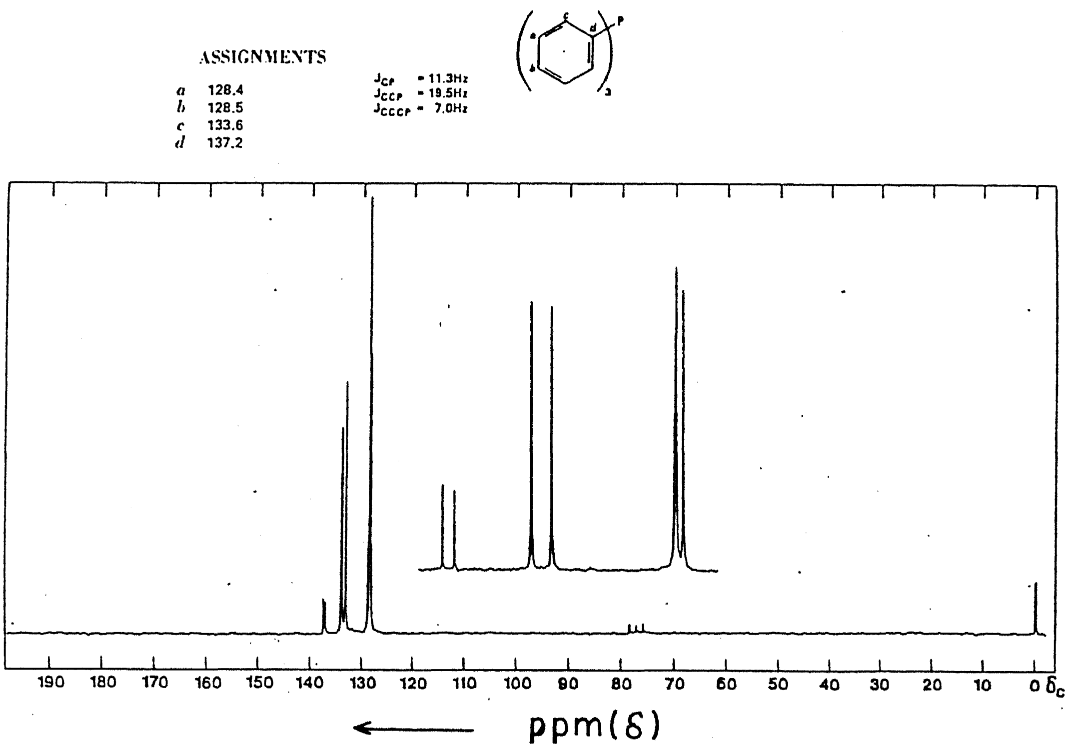


Figure 1.2. The ^{13}C NMR spectrum of triphenylphosphine.[77]

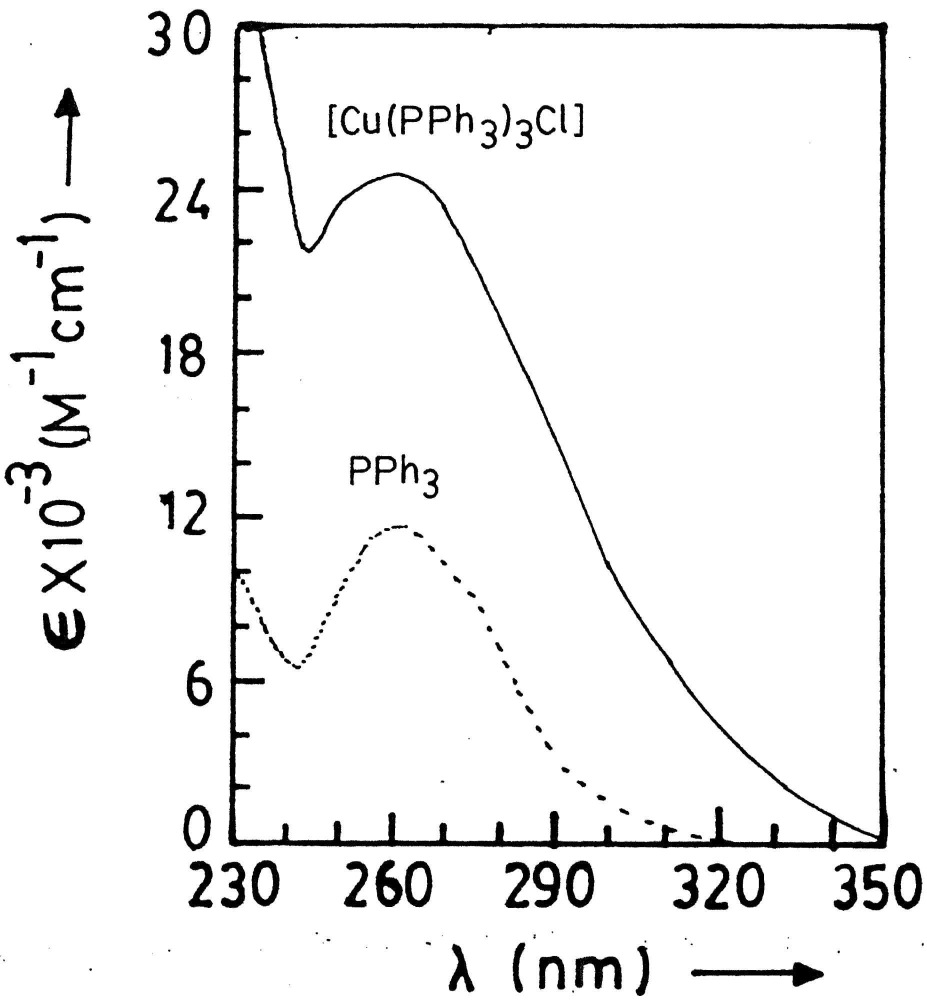


Figure 1.3. The electronic (UV-vis) spectra of PPh_3 and $[Cu(PPh_3)_3Cl]$.[79]

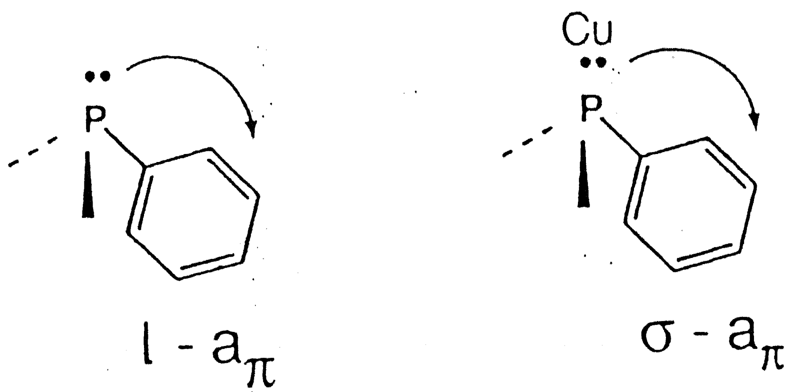


Figure 1.4. Pictorial representation of $l \longrightarrow a_\pi$ transition in arylphosphine molecules and the $\sigma \longrightarrow a_\pi$ transition in Cu(I)—arylphosphine complexes.

d-orbitals of appropriate symmetry, a mechanism exists for delocalization of π-electron density over the entire metal-phosphine unit during a $\sigma \longrightarrow a_\pi$ transition. Comparison of the electronic spectra of PPh_3 and $[Cu(PPh_3)_3Cl]$, reveals that the change in the orbital nature of the most intense absorption band from $l \longrightarrow a_\pi$ to $\sigma \longrightarrow a_\pi$ causes a relatively minor perturbation in transition energy and band-shape, Figure 1.3. At first glance this result seems surprising, since transitions involving lone pair electrons generally shifts to considerably higher energy upon protonation or complexation of the lone pair. But this shift does not occur for the singlet $\sigma \longrightarrow a_\pi$ transition of $[Cu(PPh_3)_3Cl]$, suggesting that metal-phosphorus π-back bonding plays a role in determining the transition energy. The modified $\sigma,d \longrightarrow a_\pi$ nomenclature has been suggested to emphasize such *d*-orbital participation.

1.2.1(e) X-ray Crystal Structure of $[Cu(PPh_3)_3Cl]$

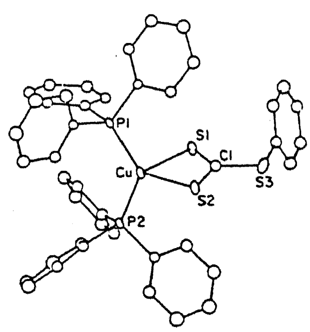
The X-ray crystal structure of $[Cu(PPh_3)_3Cl]$ is reported by Gill et al.[80] The molecular geometry is approximately distorted tetrahedral. The compound crystallizes in the trigonal space *p*3, with unit cell dimensions a = 19.2775(14) Å and c = 10.4720(9) Å, and Z = 3. A crystallographic three-fold rotation axis passes through the CuCl bond. Some important bond distances and angles are Cu—Cl(av)

= 2.34(2) Å, Cu—P(av) = 2.351(4) Å, Cl—Cu—P(av) = 109.1(7)° and P—Cu—P(av) = 109.8(7)°.

1.2.1(f) Sulphur Donor Ligand Complexes

The complexes of copper(I) with groups 14/IV, 15/V, 16/VI, and 17/VII donor atom ligands have been the subject matter of research activity for quite some time. Recently the literature has became progressively more involved in reporting copper(I) complexes of ligands containing sulphur, where sulphur may be thiolate or thione donor atom. Some of the illustrative examples are described below:

Reaction[63] of $[Cu(PPh_3)_3Cl]$ and sodium thiophenoxide yields $[Cu(PPh_3)_2SPh]$. On reaction[81] of CS_2 with $[Cu(PPh_3)_2SPh]$, CS_2 gets inserted into bond Cu—SPh. Thus, CS_2 insertion results in a trithiocarbonate copper(I) complex $[Cu(PPh_3)_2S_2CSPh]$ (**VII**) with a loss of one triphenylphosphine,



(VII)

giving a structure very similar to that reported[82] for $[Cu(PPh_3)_2(S_2CSEt)]$ which has a distorted tetrahedral structure and the thioxanthate anion acts as bidentate chelating ligand.

Reaction[83] of KOH dissolved in ROH, (R = Et, Me) with a suspension of $[Cu(PPh_3)_3Cl]$ in CS_2, yields the complex $[Cu(PPh_3)_2(S_2COR)]$, which has the structure similar to $[Cu(PPh_3)_2(S_2CSPh)]$.

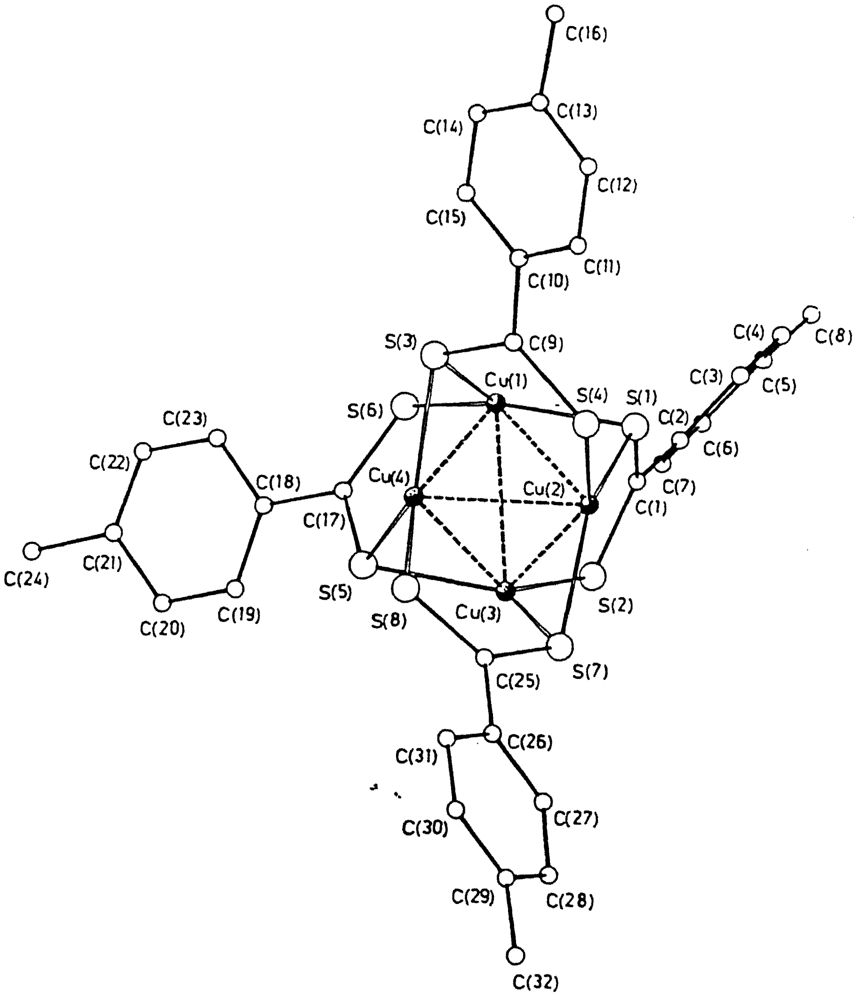
Reaction of CS_2 with $[Cu(PPh_3)_2(BH_4)]$ in dichloromethane gives $[(PPh_3)_2Cu(S_2CSCH_2SCS_2)Cu(PPh_3)_2]$. Recrystallization of this compound in CH_2Cl_2/n-heptane produces $[Cu(PPh_3)_2(S_2CH)]$ in 50% yield, whereas recrystallization in a 1:2 mixture of CH_2Cl_2/ethanol gives 25% yield of $[Cu(PPh_3)_2(S_2CH)]$ and on reducing the volume of the reaction mixture produces the precipitation of second fraction of $[Cu(PPh_3)_2(S_2COEt)]$.[84] All these compounds are having the structure similar to **(VII)**. Although in compound $[(PPh_3)_2Cu(S_2CSCH_2SCS_2)Cu(PPh_3)_2]$, the ligand acts as bridging between two metal centre, yet the mode of bonding remains same.

Reaction[83] of RMgX with a suspension of $[Cu(PPh_3)_3Cl]$ in CS_2 under stirring at 0°C produces dithiocarboxylate compound $[Cu(PPh_3)_2S_2CR]$ (R = Me). The copper(I) dithiocarboxylate complexes have been also prepared by the reaction between organo-copper(I) compounds and carbon disulphide, in which

CS_2 becomes inserted in the C—Cu bond. The reaction between ArCu (Ar = phenyl-, *m*-, *p*-tolyl etc.), suspended in toluene containing CS_2 and two equivalent of PPh_3, produces the complexes of type $[(PPh_3)_2CuS_2CAr]$.[85-87] The X-ray crystal structure of $[(PPh_3)_2CuS_2CPh]$ shows that the dithiocarboxylate group is bonded to copper as a bidentate ligand and is very similar to xanthate and thioxanthate analogues of the compound (**VII**).

The tetrameric cluster compound [CuS_2C-*p*-T]$_4$ (**VIII**) (^-S_2C-*p*-T = *p*-tolyldithiocarboxylate) is prepared[86] by the reaction between its perthio analogue and PPh_3 where upon Ph_3PS eliminates from the reaction mixture. The X-ray crystal structure of [CuS_2C-*p*-T]$_4$ reveals discrete units of four copper atoms, disposed almost at the vertices of a tetrahedron, bound to four *p*-tolyldithiocarboxylate groups acting as tridentate ligands. One sulphur atom of each ligand coordinates to only one copper atom and the other bridges two adjacent copper atoms so that each metal is in approximately trigonal planar environment of three sulphur atoms.

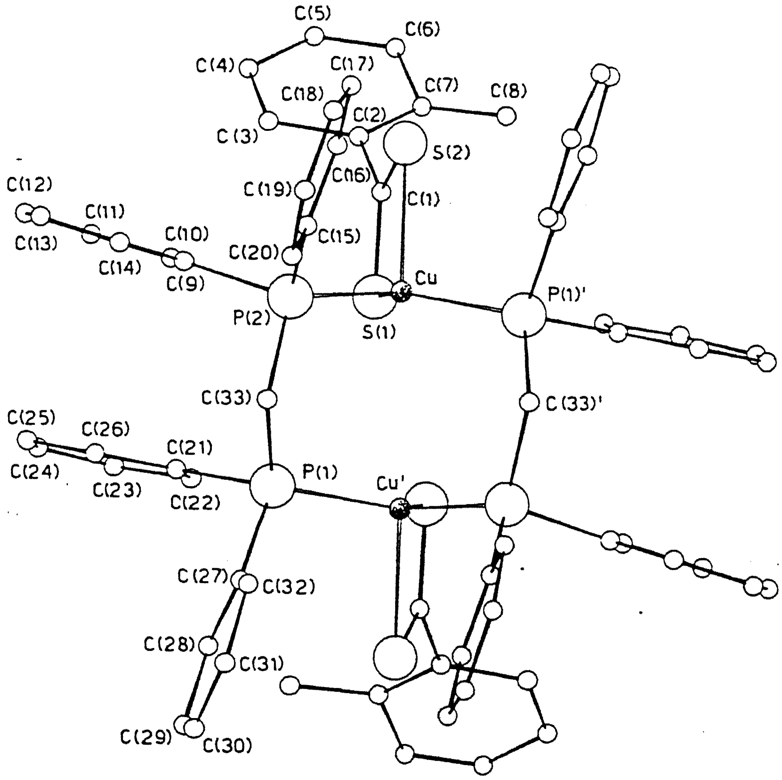
Reaction of ArCu (Ar = phenyl, *o*-, *m*-, and *p*-tolyl) with CS_2 followed by diphenylphosphinomethane (dppm) yields the dimeric compounds $[(dppm)CuS_2CAr]_2$.[88] The dimer structure of the compound [(dppm)CuS_2C-*o*-T]$_2$ (**IX**) has been confirmed by X-ray crystal structure determination,[89] in which each copper



(VIII)

atom is doubly bridged by two dppm ligands and each dithio-*o*-toluate anion acts as chelating ligand to each copper centre.

Reaction of $[CuS_2C\text{-}p\text{-}T]_4$ with excess triphenylphosphine

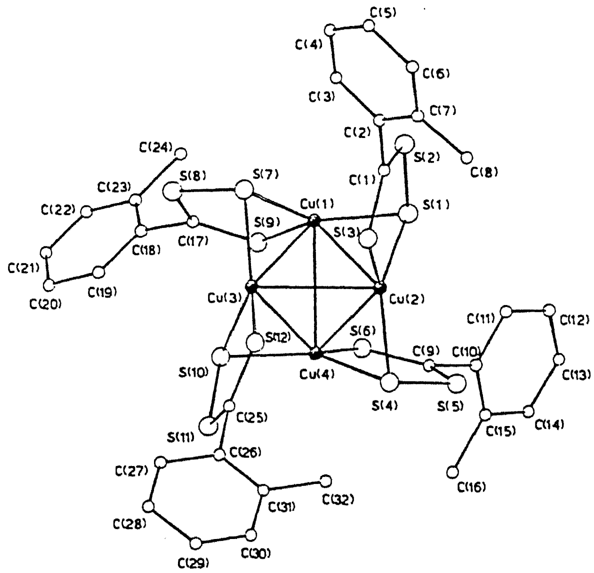


(IX)

yields $[\{Cu(S_2C\text{-}p\text{-}T)\}_4(PPh_3)_2]$,[90] having the same type of structure as the reactant, $[CuS_2C\text{-}p\text{-}T]_4$ **(VIII)**, but the two triphenylphosphine ligands are additionally attached to the two metal centres.

Reaction of a mixture of $(NH_4)_2S$, S, *o*-tolualdehyde and $CuCl_2.2H_2O$, yields the tetrameric copper(I)-*o*-tolylperthio-

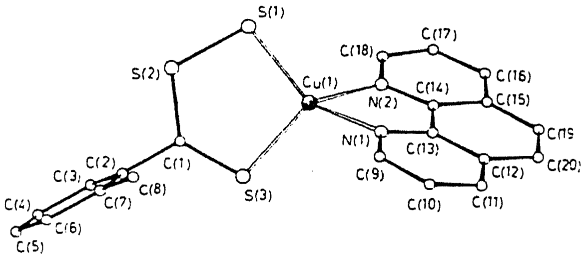
carboxylate $[CuS_3C\text{-}o\text{-}T]_4$ (X).[91,92] The crystal structure con-



(X)

sists of discrete tetramers, in which a tetrahedron of copper atoms is bonded to four *o*-tolylperthiocarboxylate ligands. Each of these ligands bridges two metal atoms through its terminal perthio atom, while the other terminal sulphur atom is coordinated only to one of these two metal copper atoms, so that five membered CuSSCS chelate rings are formed.

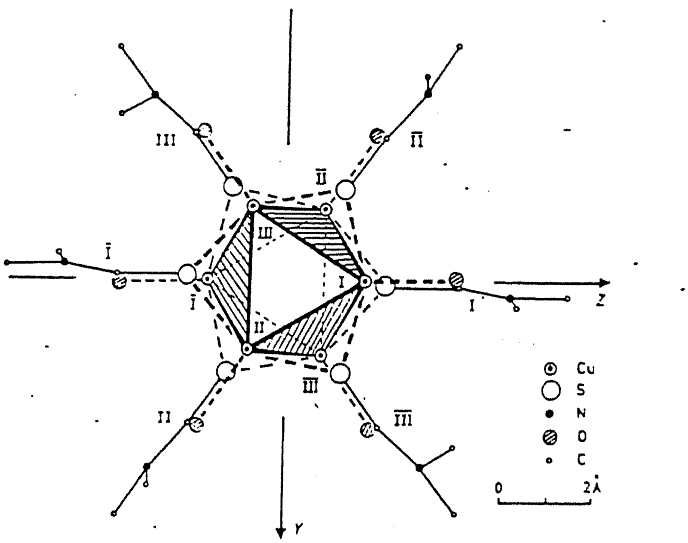
Reactions of $[CuS_2CAr]_4$ and $[CuS_3CAr]_4$ (Ar = Ph, *O*-T, *p*-T) with 1,10-phenanthroline yield $[(phen)CuS_2CAr]$ and $[(phen)CuS_3CAr]$ respectively.[93] Crystal structure of $[(phen)\text{-}CuS_3C\text{-}o\text{-}T]$ **(XI)** shows that the metal atom is pseudotetrahed-



(XI)

rally coordinated by two nitrogen atoms from phen and two sulphur atoms from the bidentate chelating *o*-tolylperthiocarboxylate ligand.

The hexanuclear copper(I) cluster $[Cu_6(mtc)_6]$ **(XII)**[94]



(XII)

(mtc = di-*n*-propylmonothiocarbamate) exhibits remarkable

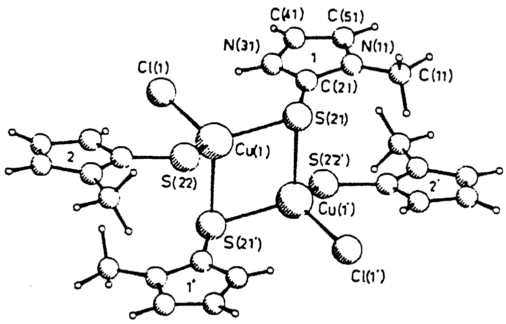
photophysical properties.[14]

The synthesis of a new type of copper(I) arenethiolates $[CuSC_6H_4[(R)\text{-}CH(Me)NMe_2]\text{-}2]_3$ and $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$, with a (chiral) intramolecularly coordinating amino group ortho with respect to the sulphur atom has been reported.[95,96] These chiral copper(I) complexes can be used as catalysts for the enantioselective, conjugated 1,4-addition reaction of organo-lithium and organo-magnesium reagents to α,β-unsaturated carbonyl compounds.[97-102] Some of the copper(I) thiolate complexes are found to be luminescent[15].

Copper(I) complexes of the thione ligands including heterocyclic thiones and aromatic thiones have been known since long time. The complexes of heterocyclic thione donors have been reviewed.[32]

Reaction of $Cu(NO_3)_2.3H_2O$ with the five fold excess amount of the thione ligand, 1-methylimidazoline-2(3H)-thione (meimtH), in refluxing condition produces the colourless crystals of tricoordinate copper(I) complex $[Cu(meimtH)_3](NO_3)$ characterized by X-ray crystallography.[103]

Copper(I) halides react with the thione ligands imidazole-2-thione ($imtH_2$), 1,3-dimethylimidazoline-2-thione (dmeimt) and meimtH to form the complexes of formula: CuL_2X (L = meimtH, dmeimt) and $Cu(imtH_2)X$ (X = Cl, Br, I).[104] The crystal structure of $[Cu_2(meimtH)_4Cl_2]$ (XIII) consists of



(XIII)

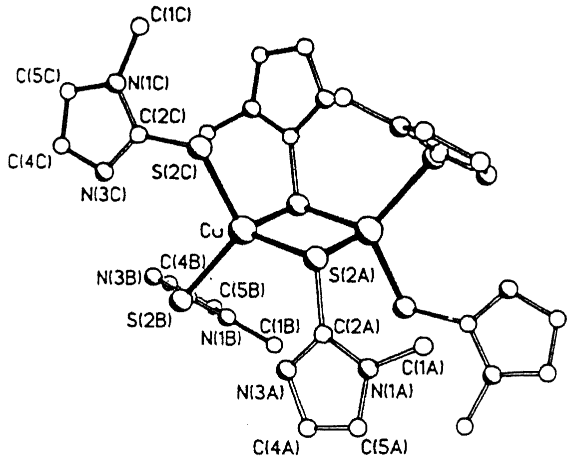
centro symmetrically constrained dimers. The dimers contain a pair of copper(I) atoms tetrahedrally coordinated by terminal chlorine and terminal S-bonded meimtH together with two S-bridging (μ_2) meimtH molecules. The bridging sulphur atom, generates a strictly planar Cu_2S_2 core, which contains alternating short and long Cu—S bonds. The terminal chlorine atoms and imido (NH) groups of the ligands form intramolecular N—H----Cl hydrogen bonds. On the basis of the crystal structure of $Cu(meimtH)_2Cl$, described above, similar structure is proposed for $Cu(imtH_2)_2X$ (X =Cl, Br, I) whereas the trigonal structure with terminal chlorine and bridging (μ_2) thione sulphur for the $Cu(imtH_2)X$ complexes are proposed. The monomeric trigonal structure for the complexes $Cu(dmeimt))_2X$ (X = Cl, Br, I), are proposed because there is no imido (NH) groups, which precludes intramolecular hydrogen

bond formation, similar to that present in $[Cu(meimtH)_2Cl]_2$, which is one of the factors helping to stabilize the dimeric form of the complexes and the tetrahedral geometry around the metal.

Reaction of meimtH with copper(II) sulphate pentahydrate in a 1:4 (metal:ligand) ratio in water-acetone mixture solvent leads to the formation of air stable copper(I) complex $[Cu_2(meimtH)_5]SO_4.3H_2O$.[26] The crystal structure determination shows the dinuclear cation, $[Cu_2(meimtH)_5]^{2+}$ which consists of two trigonal copper(I) atoms, four terminal, monodentate S-donating meimtH molecules and one S-bridging (μ_2) meimtH molecule.

Reaction between copper(II) tetrafluoroborate and meimtH in acetone-acetonitrile solution in a dinitrogen atmosphere produces a compound of empirical formula $Cu(meimtH)_3(BF_4)$.[105] The crystal structure of the compound contains centro-symmetrically constrained dimeric cations, $[Cu_2(meimtH)_6]^{2+}$ **(XIV)**, together with distorted tetrafluoroborate anions. The dimeric cations contain a pair of copper(I) atoms tetrahedrally coordinated by a pair of terminal S-bonded meimtH molecules and a pair of asymmetrically S-bridging (μ_2) meimtH molecules.

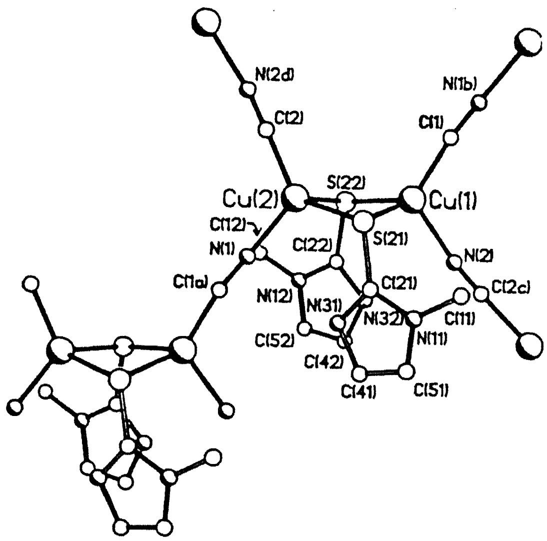
The reaction of meimtH and CuCN in aqueous KCN produces[106] colourless crystalline solid of empirical



(XIV)

composition Cu(meimtH)CN. The crystal structure shows the polymeric nature, $[Cu(meimtH)CN]_n$ **(XV)**, in which the cyanide groups bridge pairs of copper(I) atoms in a virtually linear manner. Pairs of meimtH ligands asymmetrically bridge pairs of copper(I) atoms with the production of essentially planar Cu_2S_2 cores. Each copper atom is tetrahedrally coordinated by a S_2CN donor set. The effective structural unit consists of six copper(I) atoms, four cyanide and four meimtH ligands, extended into a two dimensional array.

Reaction of meimtH and copper(I) thiocyanate in refluxing ethanol-acetonitrile solution produces a colourless, diamagnetic complex, $[Cu_2(meimtH)_4(SCN)_2]$.[107] Crystal structure shows the dimeric nature of the complex and

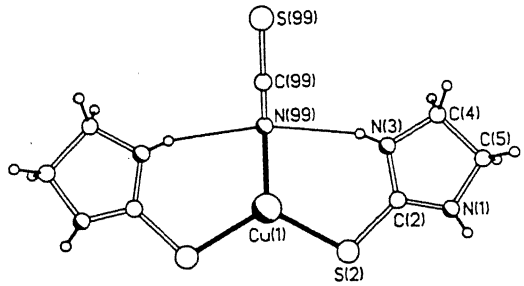


(XV)

the copper(I) atoms are pseudotetrahedrally coordinated by pairs of, asymmetrically μ_2—S bridging meimtH, terminal monodentate—S meimtH and terminal monodentate—S thiocyanate respectively. Each pair of ligands is *trans*-related to its partner across crystallographic centres of symmetry, consequently, each copper(I) atom has an identical S_4 donor set.

Reaction between copper(I) thiocyanate and 1,3-imidazolidine-2-thione ($imdtH_2$) in ethanol-acetonitrile solution

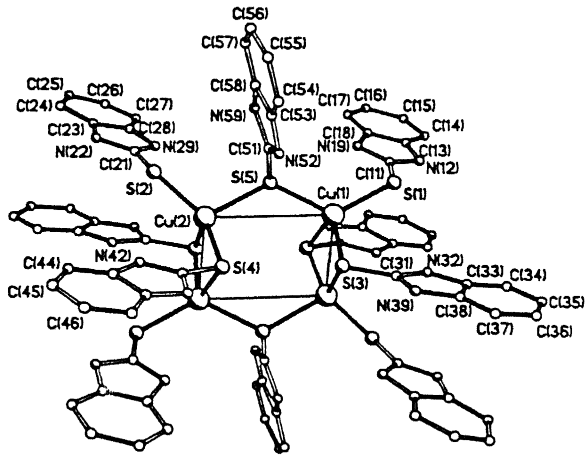
produces the compound [Cu(imdtH$_2$)$_2$(NCS)] (XVI).[108] The crystal structure of the compound shows the neutral mononucl-



(XVI)

ear nature of the molecules which contain a CuS$_2$N arrangement formed from two monodentate S-donating imdtH$_2$ ligands and an N-donating thiocyanate anion, giving a trigonal arrangement at the metal. The CuS$_2$N arrangement in the complex is further stabilized by two N—H┄N (thiocyanate) hydrogen bonds.

Reaction between copper(II) perchlorate and benzimidazoline-2-thione (bzimtH$_2$) in aqueous ethanol produces[109] a pale green crystalline solid of empirical formula [Cu$_2$(bzimtH$_2$)$_5$](ClO$_4$)$_2$.7H$_2$O. The crystal structure shows the tetranuclear nature of the complex having a planar centro symmetric array of copper(I) atoms. Each copper(I) atom is tetrahedrally coordinated by four S-donating ligands. The ten ligands in the cation [Cu$_4$(bzimtH$_2$)$_{10}$]$^{4+}$ (XVII), consists of four terminal S-donating, one asymmetric μ_2-S bridging along each of the long edges of the Cu$_4$ array and four asymmetric μ_2—S bridging ligands arranged in pairs



(XVII)

along each of the short edges of the Cu_4 array.

The copper(I) complexes[110] of 1,3-thiazolidine-2-thione (tzdtH) namely $[Cu(tzdtH)_3X]$ (X = Cl, Br, I, NO_3, ClO_4, (1/2)SO_4) have been prepared by reaction between four equivalent of tzdtH and one equivalent of CuX_2 (X = Cl, Br, NO_3, 1/2SO_4) in aqueous medium. The reaction between tzdtH and $CuSO_4$ in presence of excess of KI yields $[Cu(tzdtH)_3I]$ whereas $CuCO_3$, tzdtH and $HClO_4$ react to give $[Cu(tzdtH)_3ClO_4]$. In all these cases the anion is coordinated to the metal. Initially[110] it was proposed that in these cases the ligand tzdtH is bound to the copper(I) through its nitrogen atom, behaving as a hard-base. But later on,[111-113]

the bonding through the thione sulphur atom was established. When the ratio of CuX_2 and tzdtH is adjusted to 1:3, the tricoordinate complexes of the type $[Cu(tzdtH)_2X]$ are isolated with the same type of coordination mode.[111]

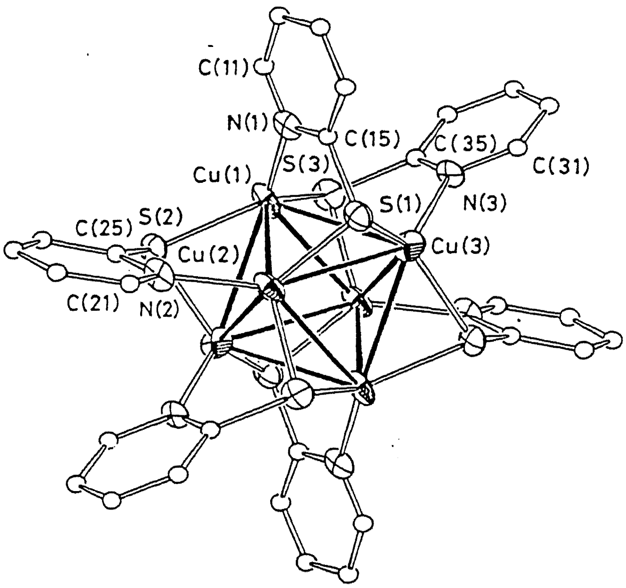
Reaction of copper(II) halides with the heterocyclic thione ligands, 1,3-oxazolidine-2-thione (oxt), pyrrolidine-2-thione (pit), N-methyl-1,3-imidazolidine-2-thione (meimdtH), $imdtH_2$ and N-ethyl-1,3-imidazolidine-2-thione (etimdtH) produces the complexes of type $[Cu_2L_4X_2]$ (L = thione ligand).[114] IR spectroscopy shows the evidence for ligand coordination to the copper(I) metal centre through thione sulphur in each case. However, the X-ray crystal structure[28] of $[Cu_2(etimdtH)_4Cl_2]$ reveals that it does not have dimeric structure, but it has monomeric compound $[Cu(etimdtH)_2Cl]$ with planar geometry and two N—H—Cl intramolecular hydrogen bonds.

The copper(I) halide (Cl, Br) complexes of the N,N′-alkyl (methyl, ethyl) substituted 1,3-imidazolidine-2-thione of the formula $[CuL_2X]$ (L = thione ligand) is synthesized[115] by treating the copper(II) halide (one equivalent) with the ligand (three equivalent) in boiling MeOH or by the reaction of stoichiometric amount of copper(II)halide and ligand.[116] The stoichiometry of the bromide complexes are very unpredictable. The X-ray crystal

structure of the complex $[Cu(dmeimdt)_2Cl]$ (dmeimdt = N,N′-dimethyl-1,3-imidazolidine-2-thione) shows the tricoordinate geometry around copper(I), involving sulphur atoms of the two ligands and one chlorine atom. As both the hydrogen atoms of the parent ligand (1,3-imidazolidine-2-thione) have been substituted by methyl group, there is no hydrogen bonding. The steric effect of the two methyls imposes a rotation of the imidazolidine rings with respect to the coordination plane. The dihedral angle between the mean plane of thiourea moieties, parallel one with the other, and the coordination plane is 119.3°.

The copper(I) complexes of deprotonated 1,3-thiazolidine-2-thione ($tzdt^-$) with copper(I) have been prepared[117] by the reaction of cupric chloride and the ligand tzdtH in 1:2 ratio in aqueous solution whose pH was maintained to prevent the precipitation of cupric hydroxide. The empirical formula proposed is Cutzdt, and on the basis of IR study and insolubility in most of the organic and water solvent, polymeric nature of the compound is suggested.

The reaction of thione ligand, 1*H*-pyridine-2-thione (py2SH), with the copper(I) complex $[Cu(MeCN)_4]PF_6$ produces the hexameric complex $[Cu_6(py2S)_6]$ (**XVIII**).[118] The single crystal diffraction study of the complex shows a discrete cluster structure consisting of deprotonated ligand $py2S^-$

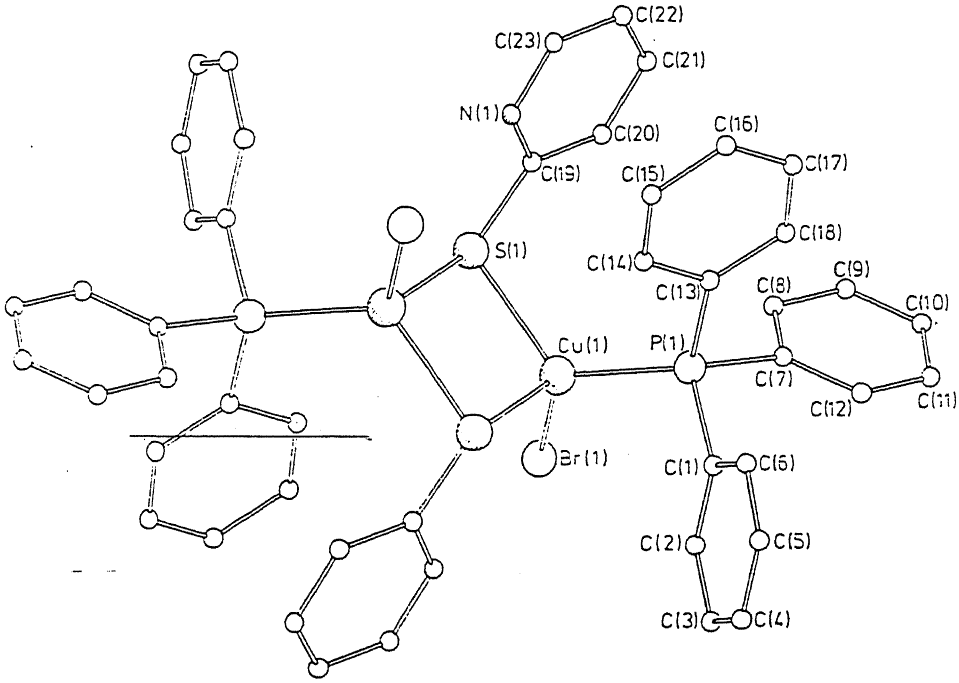


(XVIII)

each bonded to the Cu_6 core by Cu—S—Cu and Cu—N bonds, having a distorted octahedral core of six copper atoms. A very similar reaction with the thione ligand 4-hydroxy-6-methyl-pyrimidine-2-thione (Me(OH)pymtH) produces[119] same type of the hexanuclear cluster with anti-prismatic copper core of six copper atoms.

In the recent years the mixed ligand copper(I) complexes of heterocyclic thione ligands containing H—N(|)—C(|)=S group, halides, and triarylphosphine or triarylarsine have attracted

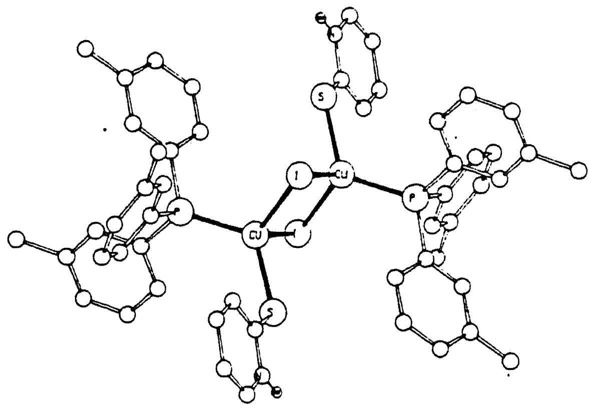
much attention. Reaction between copper(I) complex $[Cu(PPh_3)X]_4$ (X = Cl, Br, I) and the thione ligand 1*H*—pyridine-2-thione (py2SH), 1*H*—pyridine-4-thione (py4SH) or pyrimidine-2-thione (pymtH) in 1:4 molar ratio yields the dimeric complex having general formula $[Cu(L)(PPh_3)X]_2$[29] (L = thione ligand). The crystal structure of $[Cu(py2SH)(PPh_3)$-$Br]_2$ **(XIX)** shows that the complex is dinuclear and stereochemistry of Cu_2S_2 is strictly planar. The equivalent copper atoms have pseudotetrahedral geometry and the sulphur atom of each thione ligands bridges (μ_2-S) the copper centres. Following the same procedure, reactions of $[Cu(PR_3)X]_4$ (PR_3 = tri-*p*-tolylphosphine (tptp), X = Cl, Br, I; PR_3 = PPh_3, X = Cl) with heterocyclic thiones (L) (L = benz—1,3—thiazoline—2—thione (bztztH), dithiouracil (dtu), purine—6—thione (pur6SH), thiourea (tu), py2SH, pymtH, tzdtH, meimtH, $bzimtH_2$ and quinoline—2—thione (qn2SH)) yield the same type of binuclear complexes of the general formula $[Cu(tptp)(L)X]_2$.[67,69] The crystal structures of $[Cu(tptp)(pymtH)Cl]_2$[67] and $[Cu(tptp)(tzdtH)Cl]_2$[69] show the same type of stoichiometry and geometry as for **(XIX)** and the two intramolecular NH——Cl hydrogen bonding per molecule of the complex. The structures of $[Cu(tptp)(pymtH)Cl]_2$ and $[Cu(tptp)(tzdtH)I]_2$ are similar to **(XIX)**, whereas the complexes having general formula $[Cu(tmtp)(L)I]_2$ (tmtp =



(XIX)

tri-*m*-tolylphosphine; L = py2SH, pymtH, tzdtH, meimtH, $bzimtH_2$, qntH) are having entirely different mode of coordination in which the iodine atoms act as bridging ligands between two metal centres. This is revealed by the X-ray crystal structure of $[Cu(tmtp)(py2SH)I]_2$ (XX).[71]

Reactions of $[Cu(totp)X]_4$ (X = Cl, Br, I; totp = tri-*o*-tolylphosphine) with heterocyclic thiones (L) (L = py2SH, pymtH, tzdtH, meimtH, $bzimtH_2$, qntH) afford mononuclear complexes of general formula [Cu(totp)(L)X].[72,74] A single X-ray crystal structure of the complexes

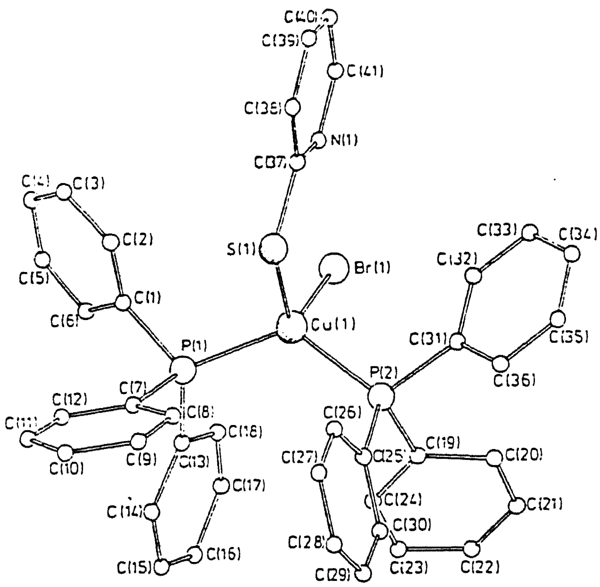


(XX)

[Cu(totp)(pymtH)Cl], [Cu(totp)(tzdtH)X] (X= Br, I) shows the trigonal planar geometry of CuSPX core with a NH----X hydrogen bond. The mononuclearity of the complex is because of the steric factor of the ortho positioned methyl groups of phosphine ligand.

The steric effects of the two bulky ligands in the complexes[75] [Cu(Pcy_3)(tclH)X] (Pcy_3 = tricyclohexylphosphine, tclH = ω—thiocaprolactam, X = Cl, Br, I) are responsible for their mononuclearity and tricoordination. These complexes are synthesized by reaction of CuX, tclH and Pcy_3 in 1:1:2 ratio in chloroform-acetonitrile mixture.[75]

Reaction between Zr(py2S)$_4$ and [Cu(PPh_3)$_3$Br] in 1:4 molar ratio yields the monomeric complex [Cu(PPh_3)$_2$(py2SH)-Br][29] **(XXI)** having distorted tetrahedral geometry and the



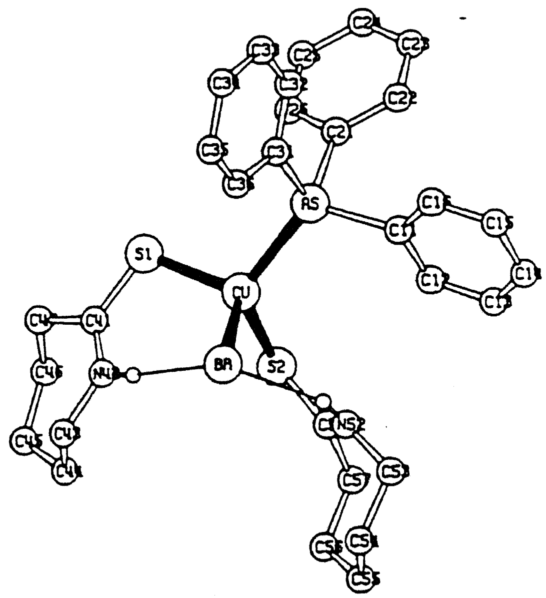
(XXI)

thione ligand binds through the sulphur atom.

Reactions of copper(I) bromide with heterocyclic thiones (L) (L = tzdtH, meimtH, bzimtH_2, benz-1,3-oxazoline-2-thione (bzoxtH), 5-nitro-2-benz-1,3-imidazoline-2-thione (nbzimtH_2), benz-1,3-thiazoline-2-thione (bztztH), quinazolinone-2-thione (qnotH_2), py2SH, Py4SH and pymtH) in the presence of triphenylphosphine yield mononuclear complexes of the general formula $[Cu(PPh_3)_2(L)Br]$.[65] The crystal structure of $[Cu(PPh_3)_2(pymtH)Br]$ shows the distorted tetrahedral environment around copper(I) and the thione ligand binds through its sulphur atom. Following the similar method of

preparation, the complexes $[Cu(PPh_3)_2(L)X]$ (L = 1-methyl-1,3-imidazoline-2-thione (meimtH), 5-methyl-2-benz-1,3-imidazoline-2-thione ($mebzimtH_2$), pur6SH, qn2SH, and X = Cl, Br, I) have been synthesized and the X-ray crystal structure of $[Cu(PPh_3)_2(meimtH)Br]$ reveals the same types of stoichiometry and geometry.[62]

Reaction of a mixture of CuX (X = Cl, Br, I), EPh_3 (E = P, As) and the thione ligand hexamethylene-imine-2-thione (tclH) in 1:1:2 ratio produces the complexes of general formula $[Cu(EPh_3)(tclH)_2X]$.[68] X-ray crystal structure of the complex $[Cu(AsPh_3)(tclH)_2Br]$ (**XXII**) shows the distorted



(XXII)

tetrahedral geometry around copper(I) in which thione ligands bind through their thione sulphur atom and the two hydrogen bonds NH----Br per molecule of complex are observed. When the ratio of CuCl:PPh_3:thione ligand is changed to 1:2:1, the complexes of general formula $[Cu(PPh_3)_2(L)Cl]$ (L = $bzimtH_2$, $nbzimtH_2$) are obtained.[70] The crystal structure of these complexes shows the distorted tetrahedral geometry with an N—H----Cl hydrogen bond.

The reaction of $[Cu(AsPh_3)_3X]$ (X = Cl, Br) or $[Cu(AsPh_3)I]_4$ with tclH in acetone or by the addition of $AsPh_3$ to $[Cu(tclH)_2X]$ in methanol/chloroform, produces the complexes of general formula $[Cu(AsPh_3)_2(tclH)X]$.[73] The crystal structure of $[Cu(AsPh_3)_2(tclH)Br]$ shows the distorted tetrahedral environment and the thione ligand binds through its sulphur atom to copper(I).

1.2.2 Reactivity of Copper(I) towards 2,2'-bipyridine and 1,10-phenanthroline

Reaction of CuCN with 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) produces the complexes [(phen)CuCN] and [(bpy)CuCN] respectively.[120] The crystal structure of $[(dmphen)CuCN]_n$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) shows that it is polymeric and has one-dimensional zigzag chains of tetrahedral copper(I) atoms linked by cyanide group.[121] The position of the bands assigned to ν(CN)

stretching modes of the anion CN^- is consistent with the bidentate nature. The two bands at 2085 and 2096 cm^{-1} are assigned to the vibrations A_g and B_g.[121]

The reactions of CuX (X = Cl, Br, I) with bpy and phen afford the dimeric complexes $[Cu(N—N)X]_2$ (N—N = phen, bpy) in acetone but $[Cu(N—N)_2]X$ are produced in ethanol solution.[122] In the dimers halogens are bridged between two metal centre giving distorted tetrahedral environment around each copper(I) centre.

Reaction of $CuSO_4.5H_2O$ with 2,9-dimethly-1,10-phenanthroline (dmphen) in 1:1 water-methanol mixture containing dissolved $NaBF_4$, and addition of ascorbic acid for reduction of copper(II) to copper(I), produces the complex $[Cu(dmphen)_2]BF_4$.[123]

Reaction of $[Cu(PPh_3)_4]BF_4$ with equivalent amount of dmphen produces the mixed ligand complex $[Cu(dmphen)(PPh_3)_2]BF_4$.[124,125] Photophysical studies of these and related complexes have shown remarkable photoemissive properties.[124-132]

Reaction of $[Cu(CH_3CN)_4]ClO_4$ with equivalent amount of bpy and the ligand L (L = $P(C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_4H_9)_3$ and $P(OC_6H_5)_3$) produces the mixed ligand complexes of type $[Cu(bpy)L_2]ClO_4$.[133]

The mixed ligand complexes $[Cu(N—N)(PPh_3)X]$ (X = Cl,

Br, I) have been prepared by two routes:[62] (a) reaction between $[Cu(PPh_3)X]_4$ and the bidentate ligands N—N (b) reaction between $[Cu(PPh_3)_3X]$ and the bidentate ligands N—N. In these complexes N—N act as bidentate ligands and the environment around copper(I) is found to be distorted tetrahedral.

Reaction of a mixture of $[(bpy)_2Ru(bpym)](PF_6)_2$ (bpym = 2,2'-bipyrimidine), copper powder, $Cu(BF_4)_2$, PPh_3 and NH_4PF_6 produces the heterobimetallic compound $[(bpy)_2Ru(\mu\text{-}bpym)\text{-}Cu(PPh_3)_2](PF_6)_3$ in which the tetradentate ligand bpym acts as bridging ligand.[134]

1.2.3 Dichlorobis(2,2'-bipyridine)ruthenium(II), $[Ru(bpy)_2Cl_2]$[135]

1.2.3(a) Synthesis and Reactivity[136,137]

$[Ru(bpy)_2Cl_2]$ was first prepared by Dwyer et al[137] by the pyrolysis of $[Ru(bpy)_3]Cl_2$ in vacuum. It was later synthesized either by refluxing $(bpyH)[RuCl_4(bpy)]$ in DMF[138] or by reducing it with Zn/HCl.[139] The later method could also be used to prepare its other analogues.[140] It was prepared in one pot reaction by refluxing $RuCl_3.3H_2O$ with an stoichiometric amount of 2,2'-bipyridine in DMF.[141] This method was improved by Sullivan et al,[142] and is the most convenient method to get reasonably pure compound in good yield.

The two chloride groups of $[Ru(bpy)_2Cl_2]$ are labile, but the substitution of the second chloride group is relatively difficult.

$$[Ru(bpy)_2Cl_2] \xrightarrow[\text{fast}]{L} [Ru(bpy)_2(L)Cl_2]^{+} \xrightarrow[\text{slow}]{L} [Ru(bpy)_2(L)]_2^{2+}$$

Although it is sparingly soluble in cold water, yet it reacts with hot water to give soluble $[Ru(bpy)_2(H_2O)Cl]^{+}$. In very dilute aqueous solution, both of the Cl groups are substituted by water molecule giving $[Ru(bpy)_2(H_2O)_2]^{2+}$.[138,143] Various mono- and disubstituted products can be derived from other precursors *e.g.* $[Ru(bpy)_2(NO_2)Cl]$,[144] $[Ru(bpy)_2(CO_3)]$,[145] and $[Ru(bpy)_2(NO_2)_2]$,[146] etc.

1.2.3(b) IR Spectra

IR spectra of $[Ru(bpy)_2Cl_2]$ is given in Figure 1.5 in which bands are mainly due to the bpy ligand vibrations.

1.2.3(c) ^1H NMR spectra

^1H NMR Spectra of $[Ru(bpy)_2Cl_2]$ in dmso-d_6 is shown[147] in Figure 1.6.

1.2.3(d) Electronic (UV-vis) Spectra[139,148]

The electronic (UV-vis) spectra of $[Ru(bpy)_2Cl_2].2H_2O$ is shown in Figure 1.7. This complex shows four characteristic bands at 550, 378, 297 and 242 nm denoted from I to IV in

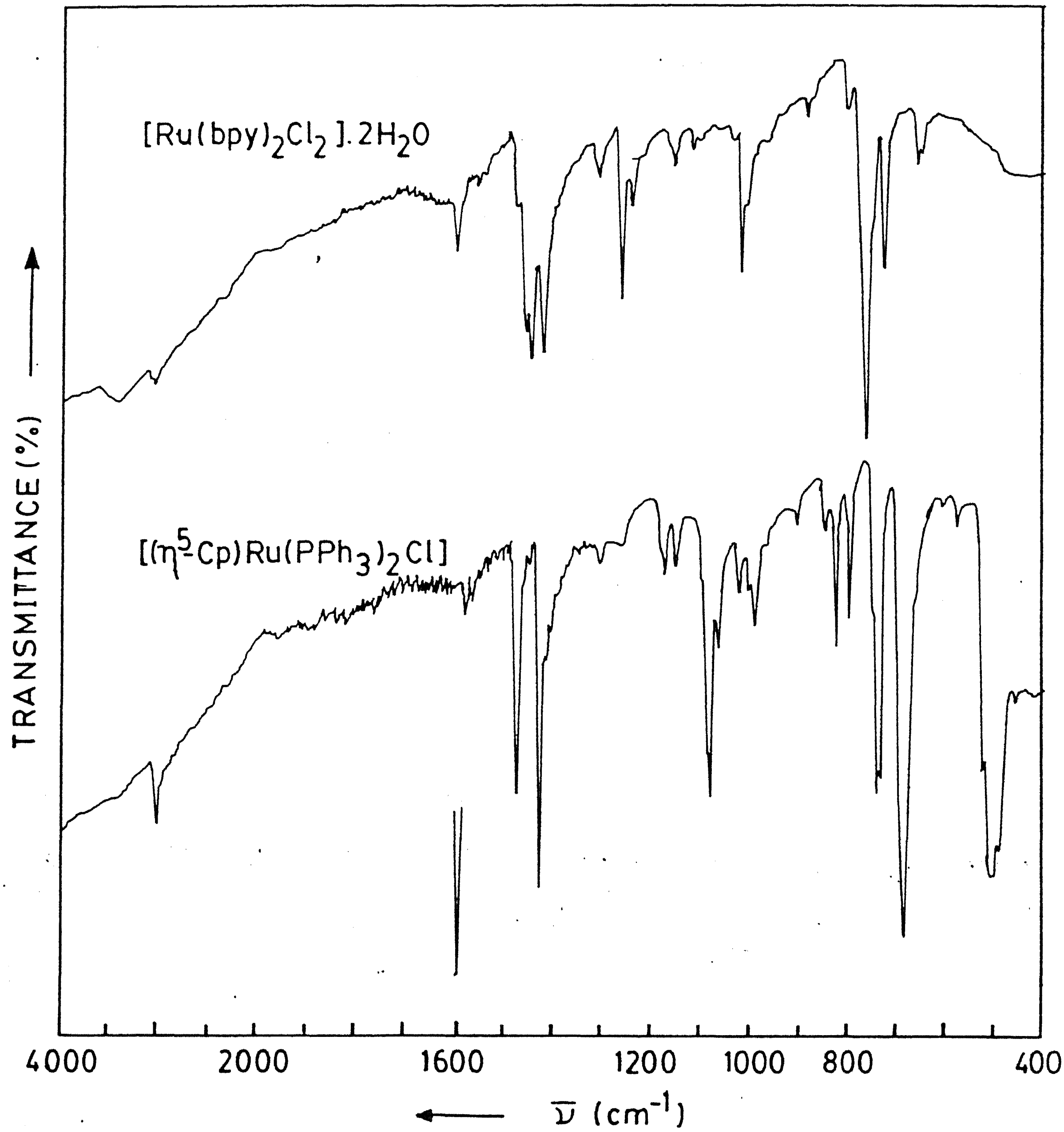


Figure 1.5. The IR spectra of the complexes $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ and $[(\eta^5\text{-}Cp)Ru(PPh_3)_2Cl]$.

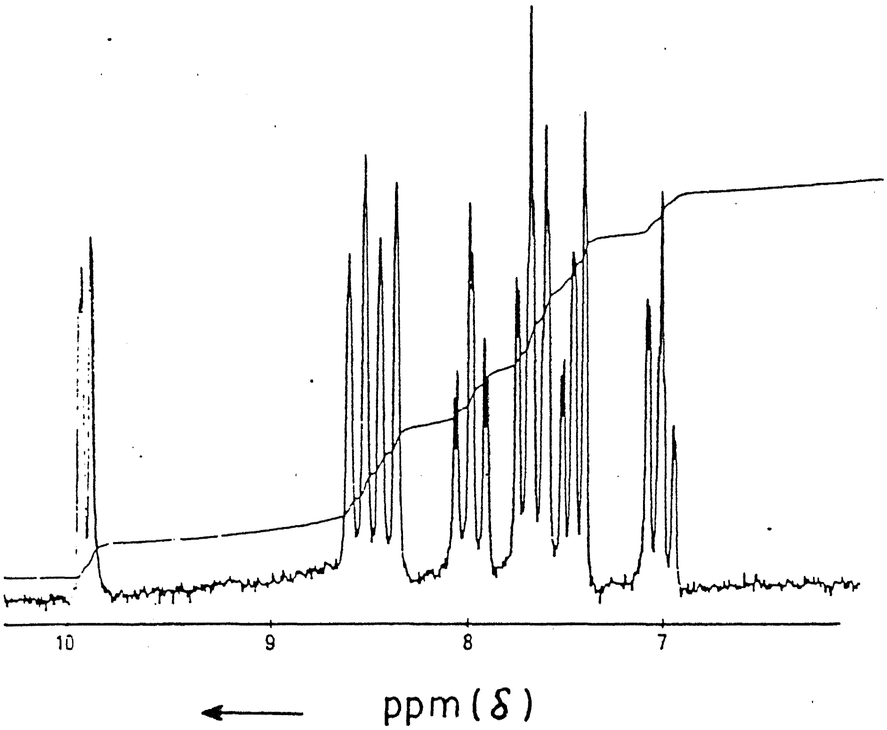


Figure 1.6. The aromatic region of the 100 MHz ^{1}H NMR spectrum of $[Ru(bpy)_2Cl_2]$ in dmso-d_6.[147]

Figure 1.7, in the UV-vis region. These bands are assigned[142,149,150] as I and II $\pi^*(bpy) \longleftarrow d_\pi(Ru)$ charge transfer transitions, whereas III and IV as $\pi^* \longleftarrow \pi(bpy)$, intraligand transitions. The lowest energy $\pi^*(bpy) \longleftarrow d_\pi(Ru)$ charge transfer band appears at 505 nm in $[Ru(bpy)_2(CN)_2]$, at 480 nm in $[Ru(bpy)_2(CH_3CN)Cl]^+$, and at 426 nm in $[Ru(bpy)_2(CH_3CN)_2]^{2+}$.[148]

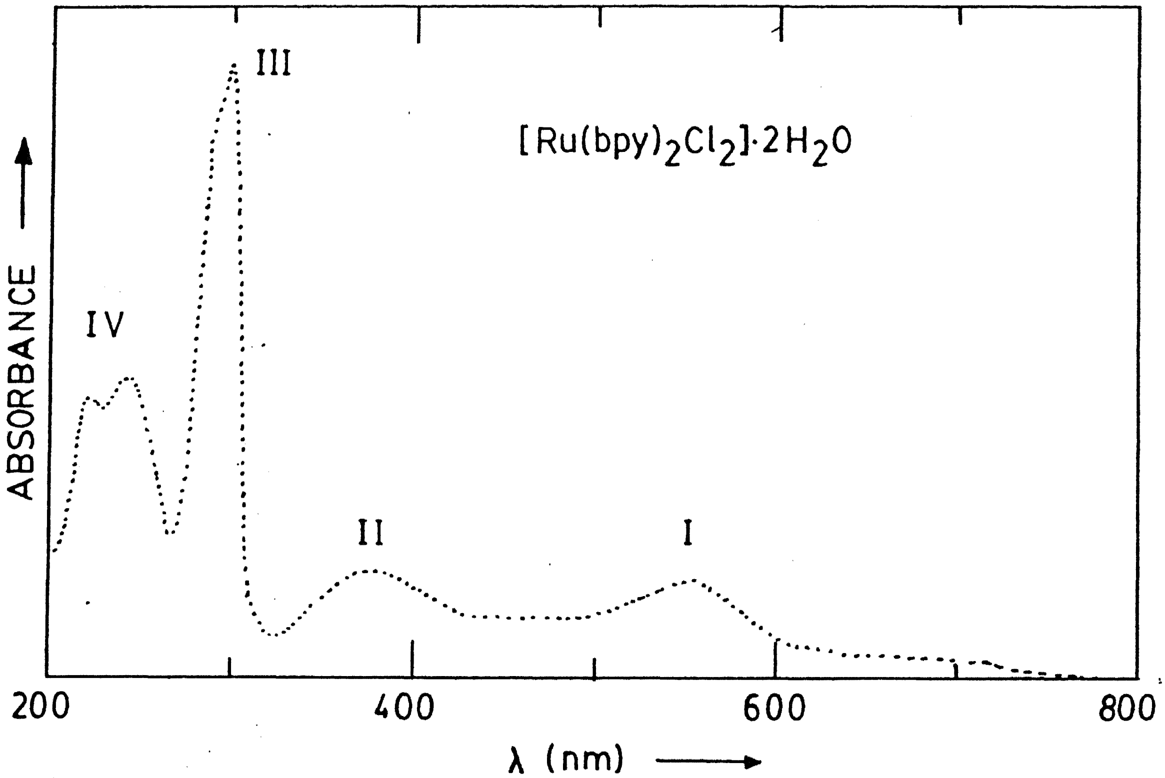


Figure 1.7. The electronic (UV-vis) spectrum of the complex [Ru(bpy)$_2$Cl$_2$].H$_2$O

1.2.4 Chlorocyclopentadienylbis(triphenylphosphine)ruthenium (II), $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$

1.2.4(a) Synthesis and Reactivity[151-154]

Orange crystalline compound $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ was first prepared by the reaction of $[Ru(PPh_3)_3Cl_2]$ and cyclopentadiene,[155] and later by the reaction of thallium(I) cyclopentadienide (TlCp) with ruthenium complexes.[156] However, the best route of synthesis is by adding a mixture of hydrated $RuCl_3$ and cyclopentadiene to an excess triphenylphosphine solution in ethanol.[157-160] All the halides[161] and cyanide[162] complexes are known. The displacement of chloride group in $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ is very facile. In methanol the following equilibrium occurs to the right.[163]

$$[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]+CH_3OH \rightleftarrows [(\eta^5\text{-Cp})Ru(PPh_3)_2(CH_3OH)]^{+}+Cl^{-}$$

The rate of solvolysis is very much dependent on the neutral ligands bound to ruthenium centre *e.g.* it is faster for PPh_3 and slowest for $PMe(OMe)_2$, indicating the dependence on the donor ability of the ligands, whereas the steric effect played practically no role. The rate of solvolysis becomes minimum when halide is substituted by π-acid ligands such as CN^-, $SnCl_3^-$ etc. The X-ray crystal structure of

$[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-Cp})Ru(PMe_3)_2Cl]$ shows that the Ru-C(ring) Ru-P and Ru-Cl bond lengths are longer in PPh_3 complexes than PMe_3 complexes, which is in accordance with the cone angle of these ligands (PMe_3 = 118°, PPh_3 = 145°).[158] For both the complexes Ru-Cl distances is relatively longer than Ru-C(ring) or Ru-P bond length. This is in agreement with the fast displacement of Cl by the neutral or anionic ligands. In the cyano-bridged dinuclear complex, Ru-CN-Ru linkage is necessarily linear, with the charge distribution $[Ru—CN—Ru]^+$.[161]

1.2.4(b) IR Spectrum

The IR spectrum of $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ is given in Figure 1.5. The major bands in the IR spectrum of $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ in the region 2500-400 cm^{-1} are 1586w, 1570w, 1434w, 1308w, 1178w, 1155w, 1087m, 1070w, 1030w, 1000w, 837w(Cp), 810w, 752m, 746m, 701s.[156] The IR spectrum analysis of the complex has not been reported so far. However, in the spectrum of ruthenocene the following bands appear.[164]

Ru-Cp(ring) stretch	446 cm^{-1}
Ru-Cp(ring) tilt	528 cm^{-1}
C-H bend (⊥)	806 cm^{-1}
C-H bend (∥)	1002 cm^{-1}

Cp ring breathing	1103 cm^{-1}
C—C stretch	1413 cm^{-1}
C—H stretch	3100 cm^{-1}

1.2.4(c) The ^{1}H, ^{31}P and ^{13}C NMR Spectra

The ^{1}H NMR spectrum, Figure 1.8, of $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ shows singlet at 4.01 ppm(δ) which is assigned to Cp protons.[156] The multiplet ^{1}H NMR signals in the region of 7.17 ppm(δ) are due to the phenyl groups of the phosphine ligands. The singlet ^{31}P NMR signal[165] is reported to be at 38.6 ppm(δ) for the PPh_3 groups. The ^{13}C NMR signal for Cp group[166-169] in the related complexes are reported in the region of 81 ppm(δ) and for the phenyl groups of phosphines[78,170,171] in the region of 125-140 ppm(δ).

1.2.4(d) Electronic (UV-vis) Spectrum

The electronic spectrum of the complex $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ is shown in Figure 1.9. Attempts for the assignments of various bands have not been made so far.[172] However, the lowest energy transition is expected due to LMCT transition. The Cp⟶Ru LMCT band in ruthenocene appears at 384.6nm.[173]

1.2.5 Cyano-bridged Complexes

The ability of the cyanide ligand carbon and nitrogen

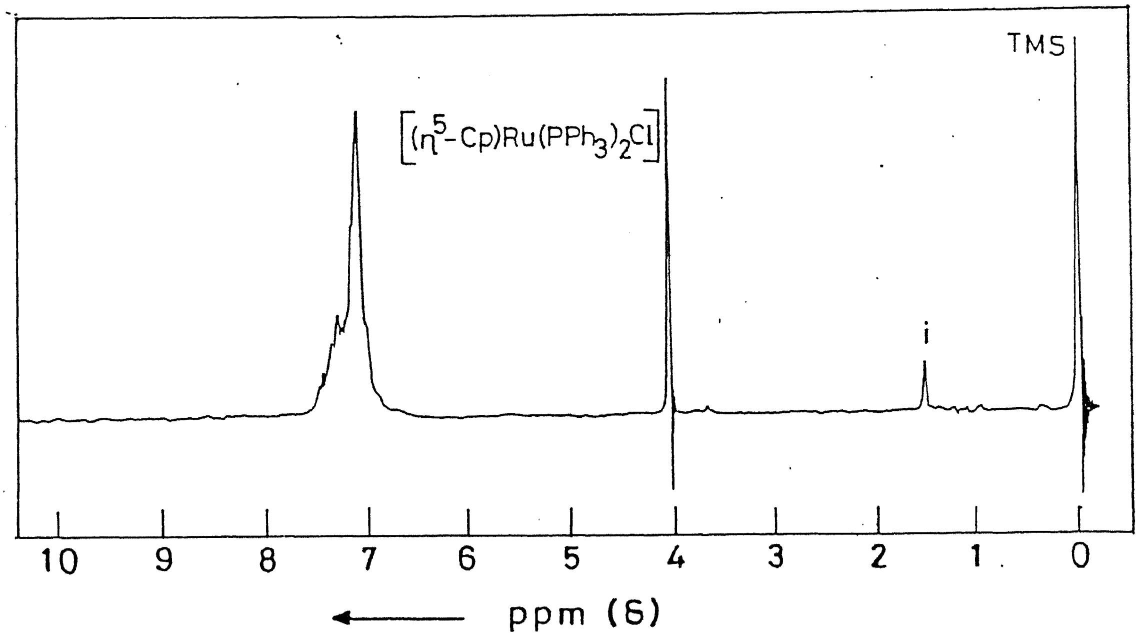


Figure 1.8. The ^{1}H NMR spectrum of the complex $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$.

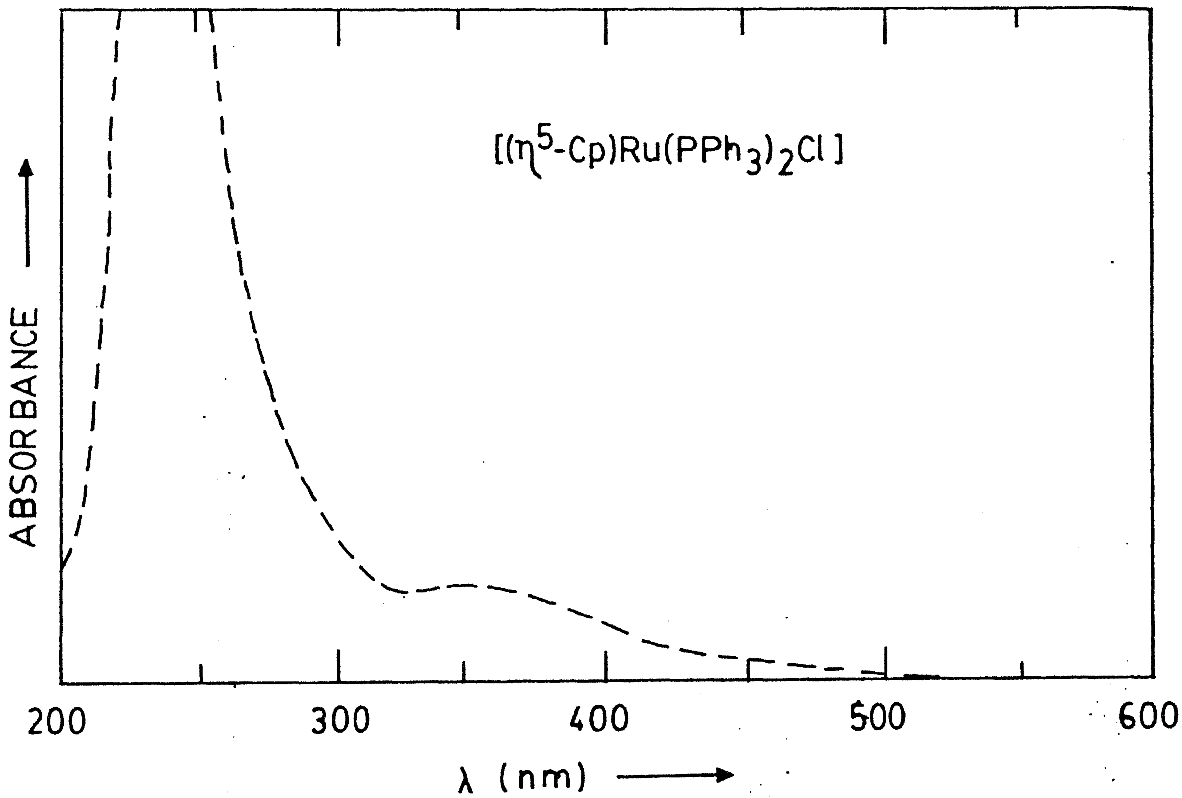


Figure 1.9. The electronic (UV-vis) spectrum of the complex $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$.

atoms to coordinate simultaneously to different metal atom centres is well documented. This ambidentate behaviour has been extensively utilized in the synthesis of polynuclear transition metal complexes. The cyano-bridged bimetal systems have been of interest since the early recognition that the ligand bridged complexes play an important role in inner sphere electron-transfer reactions. The chemistry and mixed-valence behaviour of dinuclear complexes have been deeply and elegantly probed by Henery Taube. There has been recently considerable interest in the synthesis and characterization of polynuclear transition metal complexes in which a photosensitizer moiety is covalently bound to other moieties that can function as electron donors or acceptors or as energy acceptors. The interest in the area is also related to the potential use of coordination compounds as building blocks in the design of photochemical molecular devices. In this context, a number of adducts between the *cis*-$[Ru(bpy)_2(CN)_2]$ chromophore and solvated metal ions or transition metal complexes (M_1, M_2) of the type $(bpy)_2Ru\begin{matrix}\diagup CN{-}M_1 \\ \diagdown CN\end{matrix}$, $(bpy)_2Ru\begin{matrix}\diagup CN{-}M_1 \\ \diagdown CN{-}M_1\end{matrix}$ and $(bpy)_2Ru\begin{matrix}\diagup CN{-}M_1 \\ \diagdown CN{-}M_2\end{matrix}$ have been synthesized. A few examples are given below:

(a) Reaction of $[Ru(bpy)_2(CN)_2]$ with $[Ru(NH_3)_5Cl]Cl_2$[51] and $[Ru(NH_3)_4(SO_4)py]Cl$[175] gives mixed valence cyano-bridged

emission intensity at 298K as well as at 77K. The energy of the emissions undergoes a bathochromic shift in going from mononuclear to polynuclear species, indicating that the lowest $d \longrightarrow \pi^*$ triplet excited state is on the N—bonded $Ru(bpy)_2^{2+}$ or $Ru(phen)_2^{2+}$ chromophoric unit and that intramolecular energy transfer between the C—bonded and N—bonded chromophores is very efficient. The intense metal-to-metal ($Ru^{II} \longrightarrow Ru^{III}$) intervalence transitions are observed for the singly oxidized forms (mixed-valence) of the polynuclear complexes, which indicate a high degree of electron delocalization. The lack of emission for singly oxidized forms of the complexes has been assigned to highly efficient intramolecular electron transfer quenching processes.

(c) The cyano-bridged complex $[(NC)Ru(bpy)_2(\mu\text{-}CN)Ru(dcbpy)_2(\mu\text{-}NC)Ru(bpy)_2(CN)]^{2-}$ (dcbpy = (dcbpy = 4,4′-dicarboxyl-2,2′-bipyridine) has been synthesized from the reaction between $Na_4[Ru(dcbpy)_2C_2O_4]$ and $[Ru(bpy)_2(CN)_2]\cdot 2H_2O$.[176] This complex has the central chromophoric fragment —Ru(dcbpy)— (sensitizer), which is N—bonded via cyanide to the terminal $Ru(bpy)(CN)_2$ (antenna) groups and is also having the four carboxyl groups. The mononuclear complex $[Ru(dcbpy)_3]^{4-}$ has been found to be highly efficient sensitizer for titanium-dioxide.[177] By using high surface area (roughness factor *ca* 200) polycrystalline anatase films together with

$[Ru(dcbpy)_3]^{4-}$, as a sensitizer, unprecedentedly high visible light to electric current conversion efficiencies in regenerative photoelectrochemical cells have been achieved.[178] The use of antenna-sensitizer molecular devices have been proposed as a possible strategy to increase the light harvesting efficiency of sensitized semiconductors.[176] This approach has been illustrated by the study of photophysical behaviour in solution and the photo-electrochemical behaviour on TiO_2 of trinuclear cyano-bridged complex $[(NC)Ru(bpy)_2(\mu\text{-}CN)Ru(dcbpy)_2(\mu\text{-}NC)Ru(bpy)_2(CN)]^{2-}$. Emission and excitation spectra of this complex show that the light energy absorbed by terminal $Ru(bpy)_2(CN)_2$ (antenna) groups is efficiently funneled to the central —$Ru(dcbpy)_2$— (sensitizer) fragment. Based on this antenna-sensitizer trinuclear cyano-bridged complex a high efficiency solar cell having solar-to-electric conversion efficiency of 7-12 percent depending on conditions, have been developed.[179,180]

Singly oxidized form of cyano-bridged trinuclear complexes $[(NC)Ru^{II}(bpy)_2(\mu\text{-}CN)Ru^{II}(dcbpy)_2(\mu\text{-}NC)Ru^{II}(bpy)_2\text{-}(CN)]$ and $[(H_2O)Ru^{II}(bpy)_2(\mu\text{-}NC)Ru^{II}(dcbpy)_2(\mu\text{-}CN)Ru^{II}(bpy)_2\text{-}(H_2O)]$ show intervalence transition bands in the infrared region typical of mixed valence systems.[53] The 532 nm laser photolysis studies of the parent/nonoxidized complexes show transient absorptions in the near-infrared region (600-1200

nm) with life time comparable to that of the luminescence from the lowest energy CT excited state. The near-IR absorption is attributed to the mixed valence species present during the lifetime of the CT excited state.

Dinuclear cyano-bridged complex $[(CO)_3(bpy)Re(\mu\text{-}CN)Re(bpy)(CO)_3]^+$ has been prepared by reaction between $[Ru(CO)_3(bpy)(CN)]$ and $[Ru(CO)_3(bpy)(CF_3SO_3)]$ in acetone.[52] The trinuclear isomeric cyano-bridged complexes $[(CO)_3(bpy)Re(\mu\text{-}NC)Ru(bpy)_2(\mu\text{-}CN)Re(bpy)(CO)_3]^{2+}$ and $[(CO)_3(bpy)Re(\mu\text{-}CN)Ru(dcbpy)_2(\mu\text{-}NC)Re(bpy)(CO)_3]^{2+}$ have been synthesized by the proper choice of the central and the terminal unit. In the former case reaction between $[Ru(bpy)_2(CN)_2]$ and $[Re(CO)_3(bpy)(CF_3SO_3)]$ has been carried out and in the later case reaction between $[Re(CO)_3(bpy)(CN)]$ and $[Ru(dcbpy)_2Cl_2]$ produces the desired complex.[52] The spectroscopic and photophysical properties of these complexes show that the lowest energy CT excited state (Re-bpy or Ru-bpy CT) is emissive in fluid solution. In the trinuclear complexes, intense absorption in the infrared region corresponding to intervalence transitions are reported in CT excited state and partially oxidized species. The intervalence transitions and the excitation spectra for the Ru-based emission suggest efficient occurrence of energy transfer from the CT excited state of the Re-based chromophore to the Ru-based unit in

both the complexes $[(CO)_3(bpy)Re(\mu\text{-}NC)Ru(bpy)_2(\mu\text{-}CN)Re(bpy)(CO)_3]^{2+}$ and $[(CO)_3(bpy)Re(\mu\text{-}CN)Ru(dcbpy)_2(\mu\text{-}NC)Re(bpy)(CO)_3]^{3+}$.

Reaction of $K_3[Cr(CN)_6]$ with $[Ru(bpy)_2(CN)(CH_3OH)]PF_6$ in red light, leads to the formation of cyano-bridged dinuclear anionic complex $K_2[(NC)Ru(bpy)_2(\mu\text{-}NC)Cr(CN)_5]$ whereas the reaction between $K_3[Cr(CN)_6]$ and $[Ru(bpy)_2Cl_2]$ leads to the formation of trinuclear cyano-bridged anionic complex $K_4[(NC)_5Cr(\mu\text{-}CN)Ru(bpy)_2(\mu\text{-}NC)Cr(CN)_5]$.[181] Photophysical studies of these complexes reveal that the visible light absorption by $Ru(bpy)_2^{2+}$ chromophore leads to the phosphorescence from the $Cr(CN)_6^{6-}$ luminophore. The occurrence of a fast (τ<10 ns), efficient (η = 1) intramolecular exchange energy transfer process from the MLCT triplet of the Ru(II) fragment to the doublet state of the $Cr(CN)_6^{3-}$ fragment has been observed in these complexes. Distinctive features of these chromophore-luminophore complexes with respect to the behaviour of the isolated luminophore observed are as follows:[181,182] (a) large light harvesting efficiency (antenna effect); (b) response to visible light (spectral sensitization); (c) 100% efficient population of the emitting state; (d) photostability. The excited-state absorption (ESA) spectrum of both bimetallic complexes exhibits a peculiar visible band not shown by free

$Cr(CN)_6^{3-}$. This band corresponds to intervalence-transfer transitions from Ru(II) to excited Cr(III).

The reaction between $[Co(CN)_5H_2O]^{2-}$ and $[Co(NH_3)_5$-$(CN)](ClO_4)_2$ in equivalent amount produces the neutral cyano-bridged homometallic dinuclear complex $[(NH_3)_5Co(\mu$-$CN)$-$Co(CN)_5]$.[183] Irradiation of the aqueous solution of this complex in the wavelength region 245-365 nm leads to photoaquation of the pentacyanocobaltate(II) centre, giving $[Co(CN)_5H_2O]^{2-}$ and $[Co(NH_3)_5CN]^{2+}$ as products with large quantum yields (0.2-0.3 mol/einstein). These wavelength represent ligand field (LF) excitation of the pentacyanocobaltate(III) chromophore; hence, efficient photoreaction of that centre indicates that in this case energy transfer to the lower LF states of the pentaaminecobalt(III) chromophore is at best competitive with ligand labilization.[184] In contrast, LF excitation of the former chromophore in the linkage isomer dinuclear complex $[(NH_3)_5Co(\mu$-$NC)Co(CN)_5]$ leads to very little reaction at that site. Since $[Co(CN)_6]^{3-}$ is quite photoactive under these conditions, this shows that coordination of the $[Co(NH_3)_5]^{2+}$ moiety to one cyanide group provides a new pathway for rapid deactivation of the $[Co(CN)_6]^{3-}$ LF states.

Reaction between [Pt(dien)Br]Br and $[Ru(bpy)_2(CN)_2].2H_2O$ leads to the formation of dinuclear and trinuclear

cyano-bridged heterometallic complexes $[(NC)(bpy)_2Ru(\mu\text{-}CN)Pt(dien)]^{2+}$ and $[(dien)Pt(\mu\text{-}NC)Ru(bpy)_2(\mu\text{-}CN)Pt(dien)]^{4+}$.[54] These complexes are luminescent in fluid solution, with emission wavelengths (in the 580-630 nm range) and life times (in the 60-630 ns range) depending on the solvent.

The cyano-bridged bimetallic complex $[(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5]$ has been synthesized by the reaction between $[Cr(NH_3)_5(H_2O)](ClO_4)_3$ and $K_3[Co(CN)_6]$ in 0.02 M $HClO_4$ solution (55°C, 9h).[185] The UV-vis absorption spectrum of this complex reveals ligand field (LF) band maxima at 310 and 468 nm characteristic of $Co—C_6$ and $Cr—N_6$ chromophores, respectively. Selective excitation of the $Co—C_6$ chromophore in 0.02 m $HClO_4$ solution using 313 nm irradiation results in bridging-cyanide labilization and the formation of $[Co(CN)_5H_2O]^{2-}$ (ϕ = 0.08). This cyanide quantum yield corresponds to a four-fold reduction in yield relative to that of the corresponding monometallic anion $[Co(CN)_6]^{3-}$, which shows the intramolecular $Co—C_6 \rightsquigarrow Cr—N_6$ energy transfer.

Reaction of $[Ru(bpy)_2(CN)_2]$ with $[Rh(NH_3)_5CF_3SO_3](CF_3SO_3)_2$ produces cyano-bridged di- and trinuclear complexes $[(NC)(bpy)_2Ru(\mu\text{-}CN)Rh(NH_3)_5](PF_6)_3$ and $[(NH_3)_5Rh(\mu\text{-}NC)Ru(bpy)_2(\mu\text{-}CN)Rh(NH_3)_5](PF_6)_6$ and with *trans*-$[Rh(NH_3)_4(H_2O)I]^{2+}$, *trans*-$[Rh(NH_3)_4Br_2]Br$, *trans*-$[Rh(NH_3)_4(CN)SO_3]$ and

$[Cr(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$, it produces the dinuclear complexes $[(NC)(bpy)_2Ru\{trans\text{-}(\mu\text{-}CN)Rh(NH_3)_4I\}](PF_6)_2$, $[(NC)\text{-}(bpy)_2Ru\{trans\text{-}(\mu\text{-}CN)Rh(NH_3)_4Br\}](PF_6)_2$, $[(NC)(bpy)_2Ru\{trans\text{-}(\mu\text{-}CN)Rh(NH_3)_4(CN)](PF_6)_2$ and the trinuclear complex $[(NH_3)_5Cr(\mu\text{-}NC)Ru(bpy)_2(\mu\text{-}CN)Cr(NH_3)_5](PF_6)_6$ respectively.[186] Reversible and irreversible energy flow between charge transfer and ligand field excited states of these cyano-bridged complexes have been described.

The intramolecular electron transfer in homo- and heteronuclear cyano-bridged complexes has been studied by a variety of physical methods. The mixed valence cyano-bridged homo- and heterodinuclear complexes $Na[(NH_3)_5Os^{III}(\mu\text{-}NC)M^{II}\text{-}(CN)_5]$ ($M^{II} = Fe^{II}$, Ru^{II}, Os^{II}), $K_6[(NC)_5Co(\mu\text{-}NC)Os(CN)_5]$ and $Na[(NH_3)_5Cr(\mu\text{-}NC)Fe(CN)_5]$ have been prepared.[187] In their UV-vis-near-IR spectra, metal to metal charge transfer (MMCT) absorption bands have been observed.

Recently the trinuclear complexes $[(H_2O)(bpy)Pt^{II}(\mu\text{-}NC)\text{-}M^{II}(CN)_4(\mu\text{-}CN)Pt^{II}(bpy)(H_2O)]$ (M = Fe, Ru, Os) have been synthesized[188] by the reaction of aqueous solutions of $[Pt(bpy)_2](ClO_4)_2$ with $K_4[M(CN)_6]$ according to the following stoichiometry:

$$2[Pt(bpy)_2]^{2+} + [M(CN)_6]^{4-} + (n+2)H_2O \longrightarrow \{[(H_2O)(bpy)Pt(\mu\text{-}NC)]_2M(CN)_4\}.nH_2O + 2bpy$$

This substitution reaction is certainly facilitated by the kinetic lability of one bpy ligand in the complex cation $[Pt(bpy)_2]^{2+}$.[189] The UV-vis spectrum of the trinuclear complexes are dominated by intense long wavelength absorptions at λ_{max} = 475 nm (M = Fe), 410 nm (M = Ru) and 428 nm (M = Os). These long wavelength absorptions of the trinuclear complexes are assigned to the remote MLCT transitions from M^{II} to the bpy ligands which are coordinated to Pt^{II}. This CT between remote redox sites may be facilitated by through-bond interaction via the intervening bridging cyanide and the Pt^{II} metal centre.[188]

The cyano-bridged species $[(NC)_5Fe^{II}(\mu\text{-}CN)Co^{III}(NBETA)]$ (NBETA = N—benzylethylenediaminetriacetate) and $[(NC)_5Fe^{II}\text{-}(\mu\text{-}CN)Co^{III}(HEDTA)]$ (HEDTA = N—hydroxyethylethylenediamine-triacetate) in solution have been prepared by addition of $[Fe^{III}(CN)_6]^{3-}$ to a solution containing the appropriate Co^{II} chelate (pH 6.0) until ~1% excess of $[Fe^{III}(CN)_6]^{3-}$.[190] The rate of intramolecular electron transfer in the binuclear complexes $[(NC)_5Fe^{II}(\mu\text{-}CN)Co^{III}(chelate)]$ (chelate = NBETA, HEDTA) have been measured directly using picosecond absorption spectroscopy. Excitation of the Co^{III} $^1T_{1g}\longleftarrow{}^1A_{1g}$ band by a 530 nm 6 ps laser pulse is followed by rapid electron transfer from Fe^{II} resulting in Fe^{III}, and Co^{II} in the ^2E state. It has been shown that the Co^{II} ^2E state has

~75 ps lifetime and experiences a low-spin to high-spin intersystem crossing to form the $^{4}T_{1g}$ ground state. The subsequent spin-permitted electron transfer back to the Fe^{II} species occurs in ~95 ps.

Mixing of the aqueous solution of $[Ru^{III}(NH_3)_5Cl]Cl_2$ (slightly yellow) and $K_4[Ru^{II}(CN)_6]$ (colourless), solution turns reddish immediately.[191] This red colour is caused by a new absorption band with a maximum at 510 nm. This absorption band has been assigned to an outer-sphere Ru(II) to Ru(III) IT within the ion pair $[Ru(NH_3)_5Cl]^{2+}/[Ru(CN)_6]^{4-}$. Upon irradiation of this IT band (λ_{irr}>490 nm) the solution turns blue due to the formation of the cyano-bridged complex $[(NH_3)_5Ru^{III}(\mu\text{-NC})Ru^{II}(CN)_5]^-$. This cyano-bridged complex has also been prepared and isolated by heating (60°C) the aqueous solution of $[Ru(NH_3)_5Cl]Cl_2$ and $K_4[Ru(CN)_6]$ for 2 h.[191] The blue colour of this cyano-bridged complex is assigned due to IT absorption at λ_{max} = 680 nm. Laser excitation at postresonance to this IT absorption band (λ_{ex} = 514.5 nm) leads to enhanced Raman Scattering.[192] The key feature of this Raman spectrum is that enhanced scattering is observed from both ends of the mixed-valence ion, based on a single electronic excitation *e.g.* an amine—Ru stretch occurs at 492 cm^{-1}, and C≡N stretches exist at 2077 (weak, terminal) and 2118 cm^{-1} (strong, bridging).

The bimetallic cyano-bridged complex Na[$(NH_3)_5Ru(\mu$-NC)-$Fe(CN)_5$][193] has been analogously prepared as its ruthenium homometallic analogue.[191] The direct measurement of the kinetics of intramolecular photoinduced metal to metal charge transfer (MMCT) has been made, i.e.

$$(NH_3)_5Ru^{III}(\mu\text{-NC})Fe^{II}(CN)_5^- \underset{k_{ET}}{\overset{h\nu}{\rightleftarrows}} (NH_3)_5Ru^{II}(\mu\text{-NC})Fe^{III}(CN)_5^-$$

where the solvent is H_2O or D_2O and k_{ET} signifies the reverse electron-transfer (ET) rate coefficient. The apparent reverse electron-transfer kinetics are nonexponential with a limiting rate constant $k_{lim} = k(t)$ where $t \longrightarrow \infty$, equal to $(8 \pm 3) \times 10^{11}\ s^{-1}$.[194]

The reaction of an alkylaquocobaloxime, [Co(dmgH)$_2$-(R)(H_2O)] (R = CF_3, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, C_6H_{11}), with a cyano (ligand) cobaloxime, [Co(dmgH)$_2$(CN)(B)] (B = py, py-4-NH_2, py-3-Cl, NH_3, piperidine), has been found to produce a series of cyano-bridged dicobaloximes of the general formula [R—Co(dmgH)$_2$(μ-NC)Co(dmgH)$_2$—B].[195] The thermochromic effects in this asymmetric mixed-valence system has been described.[193]

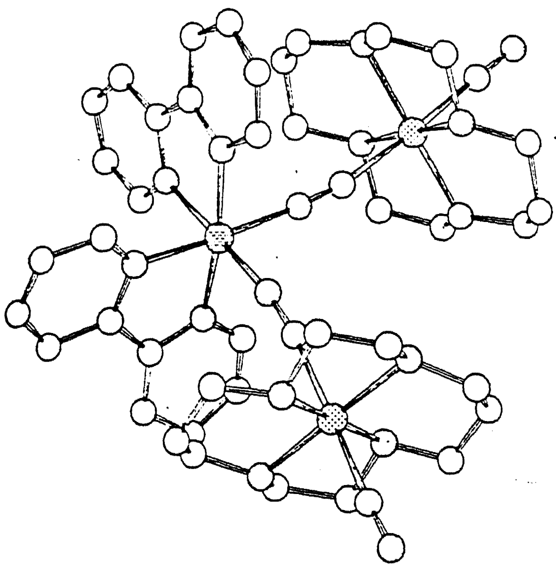
The cyano-bridged complexes [Cl(bpy)$_2$Os^{II}(μ-CN)Ru^{III}-$(NH_3)_5]^{3+}$, [(NC)(bpy)$_2$Os^{II}(μ-CN)Ru$^{III}(NH_3)_5]^{3+}$ and [$(NH_3)_5$-Ru^{III}(μ-NC)Os^{II}(bpy)$_2$(μ-CN)Ru$^{III}(NH_3)_5]^{6+}$ as PF_6^- salts, have

been synthesized[55] following the methods of preparation of the analogous complexes of ruthenium.[51,175] These complexes are also isolated as mixed valence salts with the Os^{II}-Ru^{II} forms generated in solution by the addition of hydrazine. The UV-vis spectrum of [2,3] form of the cyano-bridged complex $[Cl(bpy)_2Os^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5](PF_6)_3$ consists of a series of overlapping bands at 360, 438 and 558 nm and in the near-IR at 810 and 1168 nm in addition to the characteristic $\pi \longrightarrow \pi^*$ bands below 300 nm. Wavelength dependent Resonance Raman (RR) measurements have been successfully utilized for the assignments of such electronic transitions in complicated, overlapping absorption spectra. On the basis of such RR studies the band at 810 nm for the complex $[Cl(bpy)_2Os^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^{3+}$ has been assigned as an intervalence-transfer (IT) transition ($Os^{II} \longrightarrow Ru^{III}$).[55]

The double salts of the type *cis*-$[Co^{III}(NH_3)(en)_2(H_2O)]_2[M^{II}(CN)_4]_3$ (en = ethylenediamine; M = Ni, Pd, Pt) have been prepared and by anation in the solid state the corresponding cyano-bridged dinuclear complexes *cis*- or *trans*-$[(NH_3)(en)_2Co^{III}(\mu\text{-}NC)M^{II}(CN)_3]_2[M(CN)_4]$ have been synthesized.[196] The very similar complexes of the type *cis*-$[(NH_3)_4(H_2O)Co(\mu\text{-}NC)M(CN)_3]_2[M(CN)_4]$ and *cis*-$[(H_2O)(en)_2Co(\mu\text{-}NC)M(CN)_3]_2[M(CN)_4]$ (M = Ni, Pd, Pt) have been separated from the aqueous medium by the reaction of $[Co(H_2O)_2$-

$(NH_3)_4](ClO_4)_3$ and $[Co(H_2O)_2(en)_2](ClO_4)_3$ with $Na_2[M(CN)_4]$ respectively and by adjusting the pH of the reaction mixture which is very crucial.[197]

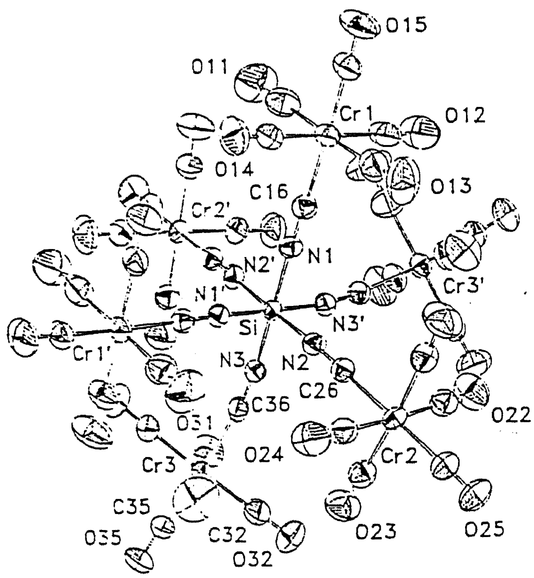
Reaction of $Ru(bpy)_2Cl_2$ with ~10 fold excess amount of $[Cr(cyclam)(CN)_2]Cl$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) produces the trinuclear cyano-bridged complex[198] $[(NC)(cyclam)Cr(\mu\text{-}CN)Ru(bpy)_2(\mu\text{-}NC)Cr(cyclam)(CN)]^{4+}$ **(XXIII)**. Visible light absorption by the $[-Ru(bpy)_2-]^{2+}$ chromophore



(XXIII)

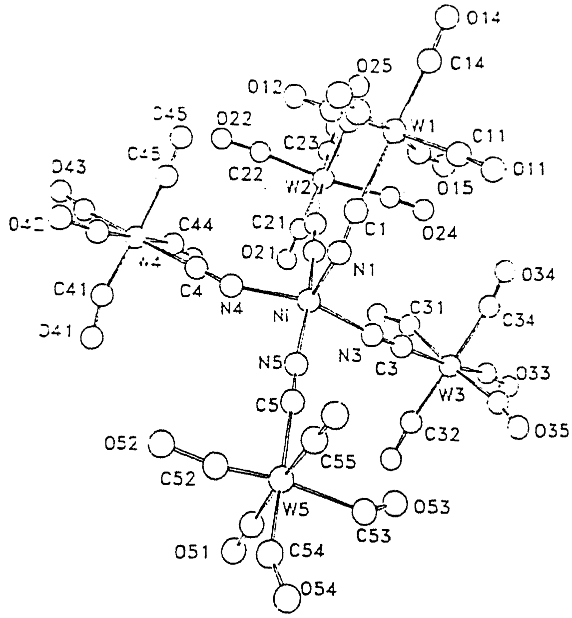
leads to emission from the $[Cr(cyclam)(CN)_2]^+$ luminophore, as a consequence of very efficient (≥99%) and fast (subnanosecond time scale) chromophore-luminophore exchange energy transfer process.[198]

A series of mostly homoleptic supercomplexes have been synthesized and characterized in which a central metaloid (Si^{IV}, Ge^{IV}, Sn^{IV}) or 3*d* metal (Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Zn^{II}) is surrounded by up to six 'ligand complexes' $[(NC)M'(CO)_5]^-$ (M' = Cr^0, Mo^0, W^0).[199] X-ray crystal structure determination of the heptanuclear six-coordinate $(NEt_4)_2[Si\{(\mu\text{-}NC)Cr(CO)_5\}_6]$ (**XXIV**), hexanuclear five-coordinate $(NEt_4)_3[Ni\{(\mu\text{-}NC)W(CO)_5\}_5]$ (**XXV**) and



(XXIV)

the (heteroleptic) tetranuclear four-coordinate $(NEt)_2[ClCo\{(\mu\text{-}NC)Cr(CO)_5\}_3]$ (**XXVI**) have shown their 'octahedro



(XXV)

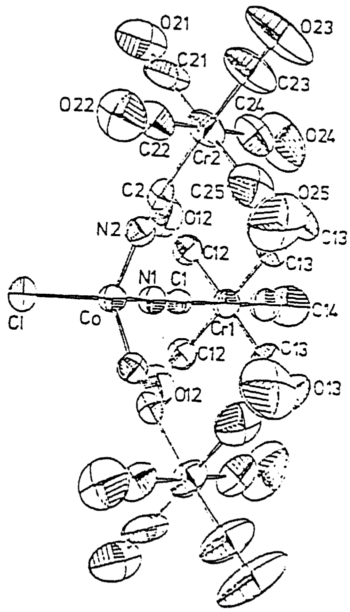
octahedron' (XXIV), square pyramidal (XXV) and distorted tetrahedron structure (XXVI) around the central metal centre respectively.

Cyanometallates $[N(PPh_3)_2][Ag(CN)_2]$ and $[N(PPh_3)_2]_2$-$[Pd(CN)_4]$ react with $SnPh_3Cl$ to produce cyano-bridged anionic complex $[N(PPh_3)_2][ClPh_3Sn(\mu\text{-NC})Ag(CN)]$ (XXVII).[200]

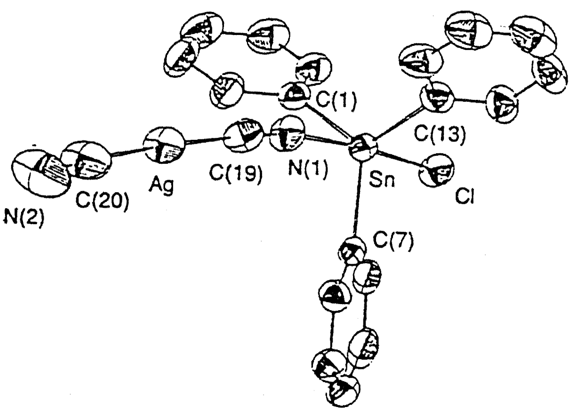
The unique cyano-bridged trimeric cyclic complex [(dppe)Pd(μ-CN)Pd(dppe)(μ-CN)Pd(μ-CN)(dppe)] (XXVIII) has been prepared by refluxing the equivalent amount of

$[Pd(dppe)(CN)_2]$ and silver perchlorate in acetonitrile.[201]

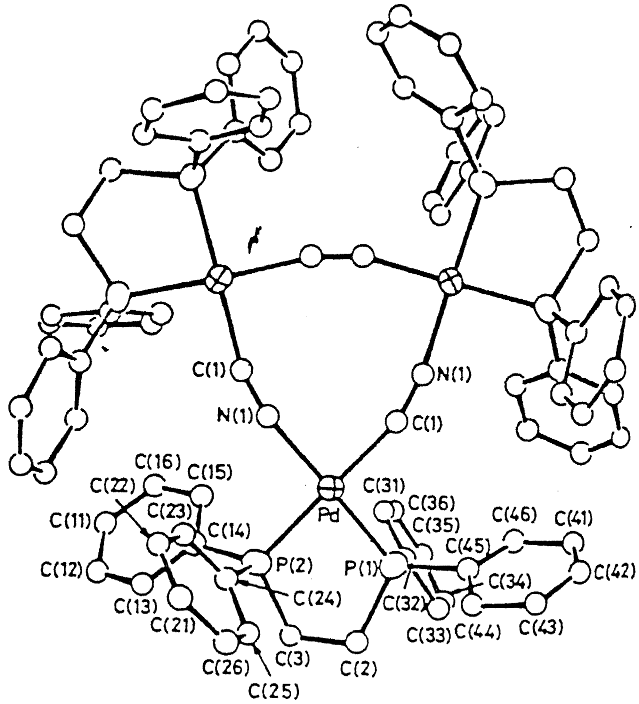
The cyano-bridged heterobimetallictrinuclear complex $[Pt(NH_3)_4]_2[(NC)_5Fe^{II}(\mu\text{-CN})Pt^{IV}(NH_3)_4(\mu\text{-NC})Fe^{II}(CN)_5].9H_2O$ (XXIX)



(XXVI)



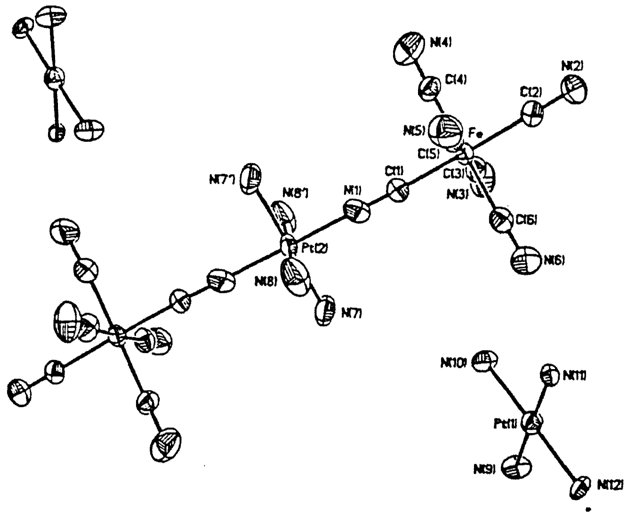
(XXVII)



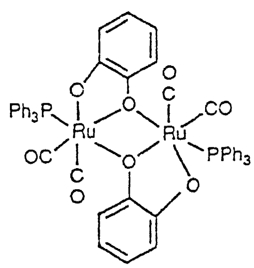
(XXVIII)

has been synthesized by the redox reaction of $Pt(NH_3)_4(NO_3)_2$ and $K_3Fe(CN)_6$ in aqueous solvent.[202] The crystal structure determination shows that the cyano-bridged Fe—Pt—Fe anion is hydrogen bonded via a terminal cyanide group on each iron atom to two separate tetrammine platinum(II) counter ions. The electronic spectrum reveals an intervalence (IT) charge transfer absorption at approximately 470 nm.

Reaction of *cis*-[$Mn(CN)(CO)_2L$(L—L)] (L = $P(OPh)_3$, L—L = dppm = $Ph_2PCH_2PPh_2$; L = PEt_3, L—L = dppe = $Ph_2CH_2CH_2PPh_2$) with [{$Ru(CO)_2(PPh_3)(\mu$-*o*-$O_2C_6Cl_4)$}$_2$] (XXX) in CH_2Cl_2 results



(XXIX)



(XXX)

in bridge cleavage of the complex (XXX) and the isolation of the orange, heterodinuclear cyano-bridged complexes.[203,204] Their redox properties have been described using cyclic voltammogram (CV) study.[203,205] Reaction of $[Mn(CN)(CO)_2L$-

(L—L)] with [BrMn$(CO)_2$L'(L'—L')] (L = L' = P$(OPh)_3$, L—L = L'—L' = dppm) in the presence of $TlPF_6$ gives homometallic dinuclear cyano-bridged complexes of the type [(L—L)L-$(OC)_2$Mn(μ-CN)Mn$(CO)_2$L'(L'—L')]PF_6 which may have *trans-trans*, *cis-trans*, *trans-cis* or *cis-cis* geometries depending on the structure of the mononuclear precursors.[206] Molecular orbital calculations[207] at the extended Hückel level have been carried out on the model homometallic dinuclear cyano-bridged cationic complexes of the type $\{[Mn](\mu\text{-}CN)[Mn]\}^+$, where [Mn] = *cis*- or *trans-mer*-Mn$(CO)_2(PH_3)_3{}^+$ and the data found are correlated to the real complexes with [Mn] = *cis*-, or *trans-mer*-Mn$(CO)_2$(L—L)L (L—L = dppm, dppe, L = PR_3, P$(OR)_3$).

The heterometallic dinuclear cyano-bridged complexes of the type $[LnM_1(\mu\text{-}CN)M_2Ln]^+$, where LnM_1 and LnM_2 are the fragments Fe(C_5H_5)(dppe) or *cis*- or *trans*-Mn$(CO)_2$(L—L) (L—L = dppm, dppe; L = P$(OPh)_3$, PEt_3) have been prepared as hexafluorophosphate salts by reaction of appropriate mononuclear complexes LnM_1—CN and X—M_2Ln (X = Br, I) in the presence of $TlPF_6$ or NH_4PF_6 as halogen abstractors.[208]

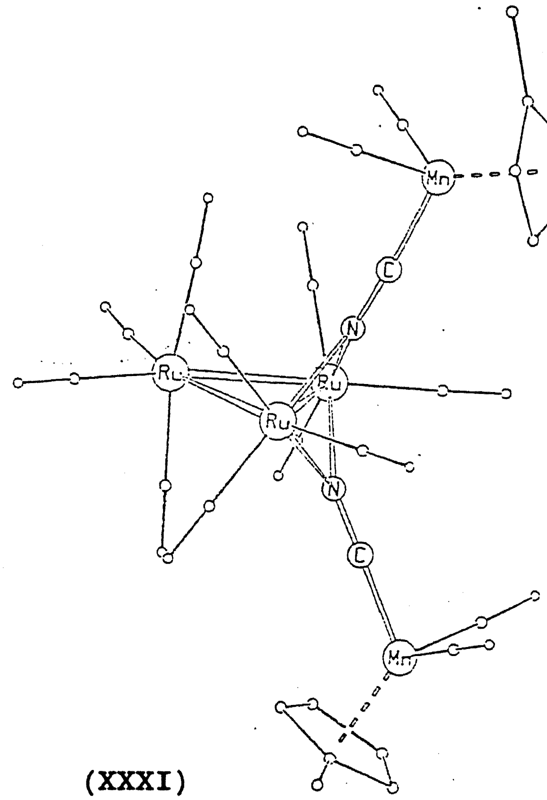
1.2.6 Cyanide Vibrations and the Cyano-bridged Complexes

Cyano complexes can be identified easily since they exhibit sharp ν(CN) in the region 2200-2000 cm^{-1}. The ν(CN) of free CN^- is 2080 cm^{-1} (water solution). Upon coordination

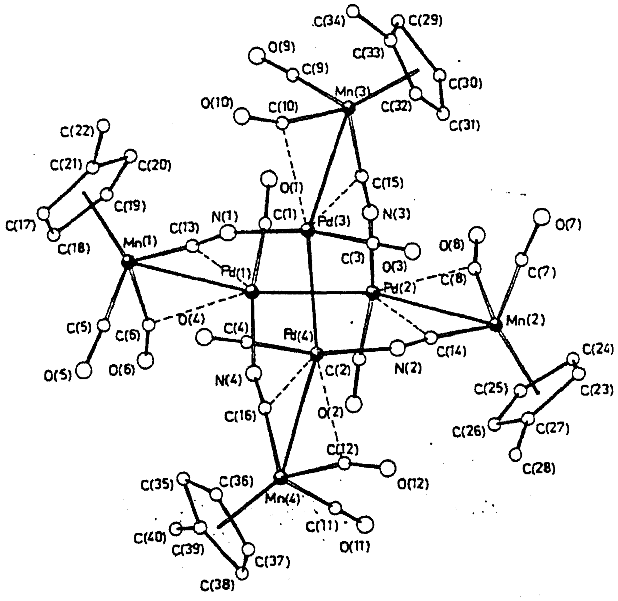
to a metal, the ν(CN) shift to higher frequencies.[209-213] The CN^- ion acts as a σ-donor by donating electrons to the metal and also as a π-acceptor by accepting electrons from the metal. The σ-donation tends to raise the ν(CN) since electrons are removed from the 5σ orbitals, which is weakly antibonding, while π-backbonding tends to decrease the ν(CN) because the electrons enter into the antibonding $2p\pi^*$ orbital. In general, CN^- is a better σ-donor and a weaker π-acceptor than CO. Thus the ν(CN) of the complexes are generally higher than the value for free CN^- which is opposite to the CO complexes.

Cyanide ion acting as a monodentate ligand always appears to have carbon as the donor atom, *i.e.* to form cyano rather than isocyanide complexes.[210] when it acts as bidentate ligand it usually does so by coordinating at both ends to form linear systems typified by Fe^{II}—CN—Fe^{III} (in Purssian blue).[214] In $CuCN.NH_3$, however, there are three Cu atoms bonded to each cyanide ion, probably one to the nitrogen and two to the carbon atom. Whereas, in the cluster complex $[Ru_3(CO)_{10}\{(\mu\text{-NC})Mn(CO)_2(\eta^5\text{-}C_5H_4Me)\}_2]$ (**XXXI**), each cyanide group is bonded with the three metal centres, two Ru and one Mn in which the nitrogen atom of the cyanide group is bonded with two Ru centre and carbon atom is bonded with Mn metal centre.[215] On the other hand in the cluster

structure (XXXII), one of the Mn-bound CO ligand is



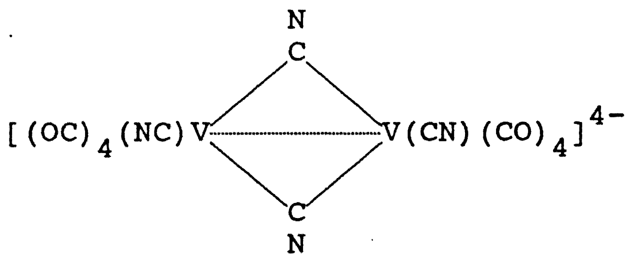
(XXXI)



(XXXII)

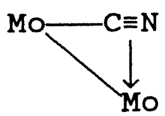
"semibridging", as indicated by the rather short contact with Pd atom, and each μ-CN ligand also makes short contacts, with a Pd atom in the neighbouring Mn—Pd—Pd—Mn chain.[216] These short contacts ("semibridging") are in a range consistent with the weak interactions between the filled π-orbitals of the nitrile functions and the empty 5*p* orbitals of the palladium atoms.[216]

The cyanide bridging[217] in the anionic complex (**XXXIII**), isolated as its tetraethyl ammonium salt, has been suggested similar to carbonyl bridging in $Fe_2(CO)_9$.



(**XXXIII**)

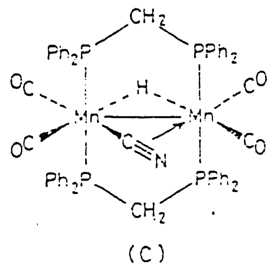
In the fluxional anion $[(C_5H_5)_2Mo_2(CO)_4(CN)]^-$, a single cyanide ion bridges the molybdenum atoms as in (**XXXIV**);



(**XXXIV**)

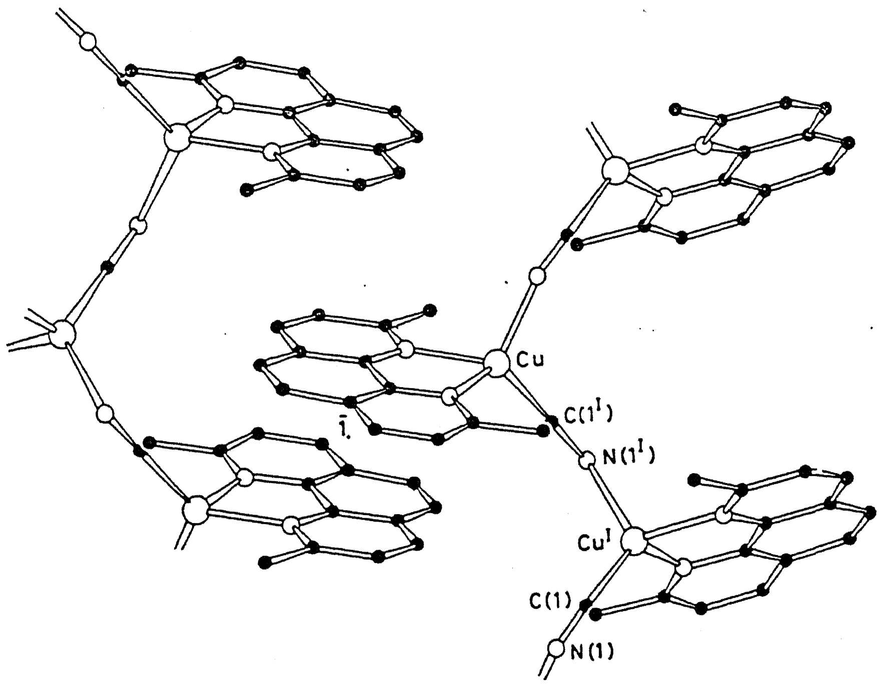
however, carbon and nitrogen atoms are not distinguished with

certainty.[218] Similar cyanide bridging is observed in the complex $[Mn_2H(CN)(CO)_4(dppm)_2$ **(XXXV)**.[219]



(XXXV)

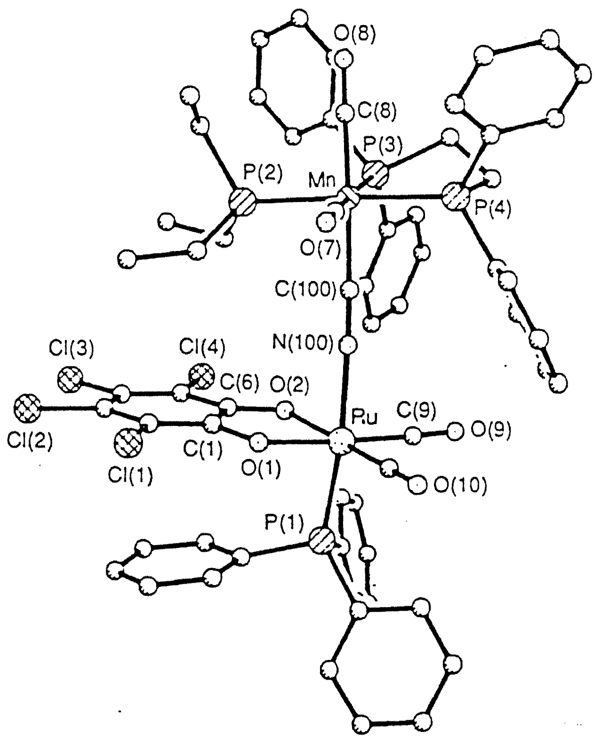
The examples of a discrete bridged group containing cyanide as a bidentate ligands are provided by the compounds **(XXVII)**,[201] $[\{Cu(dmphen)(CN)\}_n]$ **(XXXVI)**,[121] and [(dppe)-



(XXXVI)

$(Et_2P)(OC)_2Mn(\mu\text{-}CN)Ru(CO)(PPh_3)(o\text{-}O_2C_6Cl_4)]$[204] **(XXXVII)**, **(XXVII)**,[200] **(XXIX)**,[202] $(NEt_4)_2[Si\{(\mu\text{-}NC)Cr(CO)_5\}_6]$ **(XXIV)**,[199] **(XXVIII)**,[201] **(XXIII)**[198] and **(XV)**.[106]

The infrared spectroscopic studies in the cyanide



(XXXVII)

stretching region have been applied to distinguish between terminal and bridging cyanide groups. On the basis of the vibrational analysis of bridged versus non-bridged systems, it has been observed that the bridging cyanide groups exhibit a higher absorption frequency than do terminal cyanide

groups.[220,221] The ν(CN) modes of the bridging cyanide groups in the complexes $[(NC)_5Fe^{II}(\mu\text{-}CN)Co^{III}(CN)_5]^{6-}$ and $[(NC)_5Fe^{III}(\mu\text{-}CN)Co^{III}(CN)_5]^{5-}$ assigned are at much higher wave number than those for the terminal ν(CN).[221] This higher shift of ν(CN) on N—Co (bridging CN) interaction has been considered due to the donation from σ_s^* molecular orbital of cyano group to the cobalt metal centre resulting in increased C—N bond order and hence its vibrational frequency.[221,209] In the neutral cyano-bridged dicobaloximes of the general formula $[R—Co(dmgH)_2(\mu\text{-}CN)Co(dmgH)_2—B]$ (R = CF_3, CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, C_6H_{11}; B = py, py—4—NH_2, py—3—Cl, NH_3, pip), the cyanide stretching vibration, ν(CN) has been correlated with variations in the ligand R and B. The ν(CN) data show that a decrease in the σ-electron donor strength of the ligand R results in small but regular increase in ν(CN) *e.g.* when B = py—3—Cl or py; ν(CN) are 2196, 2186 and 2182 cm^{-1} for R = CF_3, CH_3 and C_2H_5 respectively.[195] The same trend for ν(CN) is observed when σ-electron donor strength of the *trans* ligand B decreases *e.g.* when R = CF_3; ν(CN) are 2196, 2192 and 2191 cm^{-1} for B = py, py—4—NH_2 and NH_3 respectively. But, the overall increase in ν(CN) on bridging in these complexes has been explained on the basis of molecular orbital theory and it has been shown that the metal-to-cyanide π-bonding is unimportant. However, the

ν(CN), ^{13}C and ^{15}N NMR studies of cyano (ligand) cobaloximes of the type [NC—Co(dmgH)$_2$—L] have produced the evidence for the cobalt-to-cyanide π-bonding and values of ν(CN) and $\nu(^{13}C^{15}N)$ tend to decrease with increasing basicity of the *trans* ligand L.[222] This and the other studies[223] on cyanide vibrations have shown the dependence of ν(CN) on the other ligands which are associated with the same metal centre. On increasing the oxidation state, the σ-donation from cyanide-to-metal centre increases, resulting in the increase of effective bond order of C—N and hence ν(CN).[209] But in the complex dication $[(\eta^5\text{-Cp})(\text{dppe})\text{Fe}(\mu\text{-CN})\text{Fe}(\text{dppe})(\eta^5\text{-Cp})]^{2+}$, the ν(CN) is observed at 75 cm^{-1} lower in frequency than that of its monocation.[208] Similar observations in decrease of ν(CN) on oxidation are found in the complexes of the type Mn(μ-CN)Ru.[204] This decrease in ν(CN) has been assigned due to the removal of the electron from the HOMO, formed by the interaction with a π-bonding orbital of the bridging cyanide and the metal centres. Therefore removal of an electron there from (HOMO) leads to weakening of the CN bond strength and hence the lower shifting of ν(CN).[207]

The lowering of ν(CN) may also be observed when there will be strong back donation from the metal-to-cyanide ligand. The two ν(CN) bands at 2085 and 2096 cm^{-1} for the

complex (XXXVI),[121] in which cyanide group is bridged between two copper(I) metal centres, are at higher frequencies than the free cyanide vibrations (2080 cm^{-1}). However, these are at much lower frequencies than the ν(CN) of the solid CuCN (2169 cm^{-1} IR, 2170 cm^{-1} Raman).[223] This may be because of the back donation from copper(I) to cyanide in the complex (XXXV), which in turn depends upon the ligating behaviour of dmphen. It may also be expected that the substitution of dmphen by a ligand having greater σ-donation property than dmphen, may cause further shifting of ν(CN) to the lower frequencies because of the enhanced back donation from copper(I) to cyanide ligand.

1.2.7 Thione Donor Ligands Containing ($H-\overset{|}{N}-\overset{|}{C}=S$) Group

Thione donor ligands containing $H-\overset{|}{N}-\overset{|}{C}=S$ group can be divided into two classes (a) cyclic thione ligands containing $H-\overset{|}{N}-\overset{|}{C}=S$ group with or without other heteroatom in the cycle (b) noncyclic thione ligands including substituted thioureas. Here is the brief account of the literature pertaining to synthetic and physical aspects of the ligands which have been studied in the thesis.

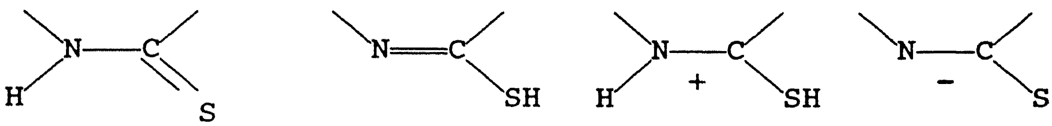
1.2.7(a) Synthesis

The synthesis of the ligands 3-phenyl-2-thioxoimidazolidine-4-one[224] (ptiH), 5-mercapto-1-phenyl-1,2,3,4-tetrazole[225] (mptH), 1-morpholinoformanilide[226,227] (mtfH),

N,N-dimethyl-N′-phenylthiourea[226] (dmptH) and N,N-dibutyl-N′-phenylthiourea[226] (dbptH) are reported in the literature. A brief description of these methods are given in chapter 2.

1.2.7(b) Tautomeric Nature of the Ligands

These are the selective ligands having H—N—C═S group and hence they can adopt either thione (**XXXVIII**) or thiol (**XXXIX**) form and by protonation or by deprotonation they can adopt protonated (**XL**) or deprotonated (**XLII**) form.



(**XXXVIII**) (**XXXIX**) (**XL**) (**XLI**)

Solid state infrared spectroscopy supports the dominance of the thione form with the presence of ν(NH) bands (*ca* 3100 cm^{-1}) and the absence of ν(SH) (*ca* 2500 cm^{-1}) and giving the characteristic "thioamide" bands.

But, in solution by changing the pH, tautomeric equilibria may be modified. In highly acidic media fully protonated species (**XL**) are likely to form. Whereas in basic media the labile N—H proton may be deprotonated, resulting in thiolate anion (**XLI**) formation which is capable of monodentate, bidentate or bridging coordination behaviour and of involving either or both sulphur and nitrogen in these processes. Many complexes of thiolate and thione forms have been reported and some of them have been characterized by

X-ray crystallography.

1.2.7(c) IR Spectra

The thione ligands and their complexes have been extensively studied by IR spectroscopy. The IR spectra of ptiH is reported[228] in the literature and the assignment[229] of the bands useful to determine the coordination site has been made. The IR spectral data of the ligand mptH are reported in the literature.[229,230] The IR spectra and the data used to decide the coordination site of the ligands are given in the respective chapters with their complexes.

The vibrational analysis on the ligand tzdtH has been reported[231] and the IR spectrum and the data useful to decide the coordination site has been given in the respective chapters along with its complexes.

The IR spectra of the ligands mtfH, dmptH and dbptH and the data useful to decide the coordination site are reported in literature[78,227,232] and given in the respective chapters along with their complexes. The various transition metal complexes of the thiourea,[232] disubstituted thioureas[233] and trisubstituted thioureas[78,227,234] have been extensively studied by IR spectroscopy. In such ligand systems IR spectroscopy has been extensively used in determining the coordinating nature of the thiones. Red shift of the thioamide bands IV and blue shift of thioamide band I are

associated with the sulphur donation whereas blue shift of the thioamide band IV and red shift of thioamide I indicates the involvement of nitrogen atom in coordination.

1.2.7(d) Electronic (UV-vis), ^{1}H and ^{13}C NMR Spectra

Electronic spectra of the ligands are given along with their complexes in the respective chapters. The ^{1}H NMR spectra of the thione ligands ptiH,[235] mptH,[236] tzdtH[78] and the substituted thiourea dmptH,[78] dbptH[78] and mtfH[237] are reported in the literature and the data are collected in the respective chapters. The ^{13}C NMR spectra of the ligand tzdtH is reported in the literature[238] and the peaks at 51.5, 33.8 and 202.0 ppm(δ) are assigned to C—N, C—S and C=S carbon atoms, respectively.

CHAPTER 2*

SYNTHESIS AND CHARACTERIZATION OF $[Cu(PPh_3)_2(LH)X]$ (LH = ptiH, mptH, mtfH; X = Cl, Br, I)

2.1 INTRODUCTION

The understanding of the stereochemistry and reactivity of copper(I) complexes, specially with the sulphur donor ligands is among the major goals of the coordination chemists, in view of the involvement of copper(I) ions in several bioprocesses. Bulky tertiary phosphine ligands exert both steric and electronic influences when they form complexes. Steric factors are frequently dominant and their influence on the course of many reactions is crucial. In order to explore the ligating behaviour of thiones and tertiary phosphines, we describe the synthesis and characterization of mixed ligands copper(I)—thione,

* R. Singh and S. K. Dikshit, *Synth. React. Inorg.-Met. Org. Chem.* **1992**, *22*, 1141.

triphenylphosphine and halide coordination compounds.

2.2 EXPERIMENTAL

2.2.1 Starting Materials

All the chemicals used are either of Analar or chemically pure grade. The copper(I) halides and the complexes of type $[Cu(PPh_3)_3X]$,[59,61,62] (X = Cl, Br or I) and the ligands 3-phenyl-2-thioxoimidazolidin-4-one[224] (ptiH); 5-mercapto-1-phenyl-1,2,3,4-tetrazole[225] (mptH) and 1-morpholinothioformalide[226,227] (mtfH) have been prepared by literature methods. The cuprous halides[239] were freshly prepared according to the literature method with a minor modification, just prior to use. A brief description of these methods is given as follows:

2.2.1(a) Copper(I) Halides

Sulphur dioxide (SO_2 was freshly prepared by adding dropwise dilute sulphuric acid to the warm aqueous solution of sodium sulphite) is bubbled through an aqueous solution (500 mL) of a mixture of $CuSO_4.5H_2O$ (50 g) and NaCl (24 g) at 60-70°C with constant stirring until white CuCl ceases to precipitate. The product is suction-filtered and washed several times with SO_2 bubbled water, three times SO_2 bubbled ethanol and ether and dried *in vacuo* over P_4O_{10} for several hours. The same procedure was followed for the preparation of

copper(I) bromide and copper(I) iodide but KBr and KI were used in place of NaCl in their respective stoichiometric amounts. The copper(I) halides are found to be air and light sensitive, hence they are stored under nitrogen atmosphere away from light to avoid any possible decomposition and they are usually freshly prepared just before use.

2.2.1(b) Tris(triphenylphosphine)copper(I)halide, $[Cu(PPh_3)_3X]$[59]

A suspension of Cu(I) halide (0.02 mol) is stirred at room temperature and then refluxed in benzene with PPh_3 (0.08 mol). The product is crystallized from the clear reaction solution by evaporation of the solvent, recrystallized two to three times from ethanol and washed with ether.

2.2.1(c) 3-Phenyl-2-thioxoimidazolidin-4-one,[224] (ptiH)

Glycine (0.01 mol) is dissolved in a 1:1 mixture of water and pyridine (50 mL). The pH of the solution is adjusted to about 9 by the addition of *N* NaOH. The solution is heated to 40°C and kept at that temperature during the reaction. Phenylisothiocyanate (2.4 mL) is added with vigorous stirring. Small portions of *N* NaOH are added to keep the pH at about 9. The reaction is completed when alkali consumption ceases.

Pyridine and excess phenylisothiocyanate are then removed by repeated extractions with equal volumes of

benzene. Subsequently, an amount of *N* HCl equivalent to the total addition of sodium hydroxide is added. This induces the precipitation of phenylthiocarbamyl (PTC) acid. The PTC acid is suspended in 30 mL of *N* HCl and refluxed for two hours. The reaction mixture is then repeatedly concentrated to dryness *in vacuo* in order to remove hydrochloric acid. Recrystallization is carried out from mixtures of glacial acetic acid and water.

2.2.1(d) 5-Mercapto-1-phenyl-1,2,3,4-tetrazole,[225] (mptH)

A mixture of phenylisothiocyanate (0.05 mol) and sodium azide (0.075 mol) is dissolved in water (100 mL) and the mixture is refluxed for a period of 4 h. The mixture is then cooled and filtered from any insoluble material present. The filtrate is then extracted twice with ether to remove any unreacted isothiocyanate present. The aqueous layer is cooled and acidified with concentrated HCl to pH 3. The precipitate obtained is filtered and washed with water.

2.2.1(e) 1-Morpholinoformanilide,[226,227] (mtfH) N,N-Dimethyl-N'-phenylthiourea[226,227] (dmptH) and N,N-Dibutyl-N'-phenylthiourea[226,227] dbptH)

These ligands are prepared by mixing equimolar quantities of the respective diamine and phenylisothiocyanate in methanol and recrystallized from acetone.

The ligand, 1,3-thiazolidine-2-thione (tzdtH) is

commercially available and used after recrystallization from hot water.

2.2.2 Physical Methods

2.2.2(a) Analysis of Copper Sulphur and Halides

Sulphur, halide and copper have been determined gravimetrically.

Estimation of Copper

A weighed amount of the complex is decomposed by digesting it with aquaregia. The digestion is continued till clear solution is obtained. This solution is evaporated to dryness repeatedly to ensure the maximum removal of acids (making up the solution each time with water). The residue is dissolved in water and filtered (solution should be either neutral or very slightly acidic). The filtrate is treated with a few drops of ethylenediamine until the characteristic coloration of the $[Cu(en)_2]^{2+}$ ion appears with a little excess of ethylenediamine, followed by the addition of solid ammonium nitrate and solid potassium iodide. The mixture is heated to boiling and a hot concentrated solution of potassium mecuri-iodide (K_2HgI_4) is added to precipitate the complex. It is allowed to cool slowly with frequent stirring. When cold, the precipitated complex $[Cu(en)_2][HgI_4]$ (en = ethylenediamine) is filtered through a previously weighed

sintered glass crucible and the precipitate is completely transferred to the crucible with the aid of a wash-liquid containing 0.1 g of mercuric chloride, 2 g of potassium iodide, 1 g of ammonium nitrate, and 2-3 drops of ethylenediamine per 100 mL, and washed several times with this solution. Final washing is done with water, ethyl alcohol and anhydrous diethylether and dried *in vacuo* for 20 minutes and weighed.

Estimation of Sulphur and Halides

The complexes are decomposed by fusing a weighed amount of the complex with $NaNO_3$ and NaOH (8 and 64 times by weight of the sample, respectively) in a nickel crucible for about 15-20 minutes. After cooling the crucible and extracting the residue with water it is neutralized with dilute HNO_3 (in case of halides) or dilute HCl (in case of sulphur) and the solution is filtered. From the filtrate sulphur is estimated as $BaSO_4$ and the halides are estimated as silver halide.

2.2.2(b) Instrumental

The carbon, hydrogen and nitrogen analyses have been done at the Microanalytical Laboratory, Indian Institute of Technology Kanpur. The IR spectra are recorded in KBr in the range 4000-400 cm^{-1} on a Perkin Elmer spectrophotometer. The electronic spectra are recorded on a Shimadzu double beam UV-160 spectrophotometer. ^1H NMR spectra are recorded on

a Jeol PMX-60 MHz spectrometer in the range 0-20 ppm(δ) in $CDCl_3$ using TMS as internal calibrant. Conductivity measurements are performed on an Elico conductivity bridge type CM 82T in acetonitrile solution. Magnetic measurements are done by using a parallel field vibrating sample magnetometer (VSM) model-150A (Princeton Applied Research Corporation, Princeton, New Jersey). Melting point of the complexes are recorded on a Fisher John melting point apparatus and are uncorrected.

2.2.3 Preparation of Compounds

To a benzene solution (50 mL) of air stable compound [$Cu(PPh_3)_3X$] (1 mmol), an equivalent amount (1 mmol) of the appropriate ligand is added and the solution/suspension is heated under reflux for about 2 h. During refluxing, the reaction mixture becomes almost clear. After cooling, the solution is filtered through a Whatman No. 1 filter paper to remove any insoluble particles. The resulting solution is concentrated under reduced pressure to half of its volume. Addition of petroleum ether (60-80°C) (100 mL) results in the precipitation of the microcrystalline products on standing for 2-3 hours. The complexes are centrifuged and washed several times with petroleum ether and dried *in vacuo*. All these air stable compounds are stored in desiccator.

Melting point, yield and colour of the complexes are

given in Table 2.1 along with the analytical data.

2.3 RESULTS AND DISCUSSION

One molecule of ligands displaces one triphenylphosphine from $[Cu(PPh_3)_3X]$ when allowed to react in benzene.

$$[Cu(PPh_3)_3X] + LH \longrightarrow [Cu(PPh_3)_2(LH)X] + PPh_3$$

Analytical data are in good agreement with the stoichiometry proposed, Table 2.1. All the compounds are air stable for several days. They are soluble in most of the organic solvents like C_6H_6, $CHCl_3$, CH_2Cl_2, DMSO, DMF, CH_3CN etc. All the compounds are diamagnetic at room temperature. The conductivity of the complexes lies in the range 50-60 $ohm^{-1}cm^2mol^{-1}$ in acetonitrile and, consequently, are interpreted according to Geary[240] as being non-electrolytes.

2.3.1 IR Spectra

IR spectra of the ligands and complexes are given in Figures 2.1, 2.2 and 2.3 and the major bands are collected in Table 2.2. All the ligands adopt the thione form both in the free state and in their complexes. This is evident by the absence of the ν(SH) band in the region of 2500 cm^{-1}, and by the presence of ν(NH) in the range[228] 2900-3300 cm^{-1}. The

Table 2.1. Analytical data of the complexes with colour, melting point (M. p.) and yield

Compound	Colour	Analytical data Found (Calculated) (%) C	H	N	Cu	S	Halide	M. p.[a] (θ/°C)	Yield (%)
(1) $[Cu(PPh_3)_2(ptiH)Cl]$	Pinkish white	66.5 (66.2)	4.9 (4.7)	3.4 (3.4)	7.8 (7.8)	3.9 (3.9)	4.5 (4.3)	165d	90
(2) $[Cu(PPh_3)_2(ptiH)Br]$	Pinkish white	62.7 (62.8)	4.6 (4.4)	3.2 (3.3)	7.7 (7.4)	3.9 (3.7)	9.0 (9.3)	190-192d	96
(3) $[Cu(PPh_3)_2(ptiH)I]$	White	59.5 (59.5)	4.2 (4.2)	3.1 (3.1)	7.2 (7.0)	3.5 (3.5)	14.1 (14.0)	175d	70
(4) $[Cu(PPh_3)_2(mptH)Cl]$	White	64.4 (64.4)	4.5 (4.5)	7.0 (7.0)	7.8 (7.9)	4.0 (4.0)	4.5 (4.4)	174d	81
(5) $[Cu(PPh_3)_2(mptH)Br]$	White	61.0 (61.0)	4.3 (4.3)	6.6 (6.6)	7.5 (7.5)	3.8 (3.8)	9.4 (9.5)	175d	85
(6) $[Cu(PPh_3)_2(mptH)I]$	White	57.9 (57.8)	4.2 (4.0)	6.0 (6.3)	7.2 (7.1)	3.5 (3.6)	14.2 (14.2)	171-172d	88
(7) $[Cu(PPh_3)_2(mtfH)Cl]$	White	66.7 (66.7)	5.2 (5.2)	3.3 (3.3)	7.5 (7.5)	3.7 (3.8)	4.2 (4.2)	153-137	83
(8) $[Cu(PPh_3)_2(mtfH)Br]$	White	63.4 (63.4)	5.0 (5.0)	3.0 (3.2)	7.2 (7.1)	3.6 (3.6)	9.0 (9.0)	152-154	90
(9) $[Cu(PPh_3)_2(mtfH)I]$	White	60.2 (60.2)	4.7 (4.7)	2.9 (3.0)	6.8 (6.8)	3.6 (3.4)	13.4 (13.5)	169-72	92

[a] d = decomposed

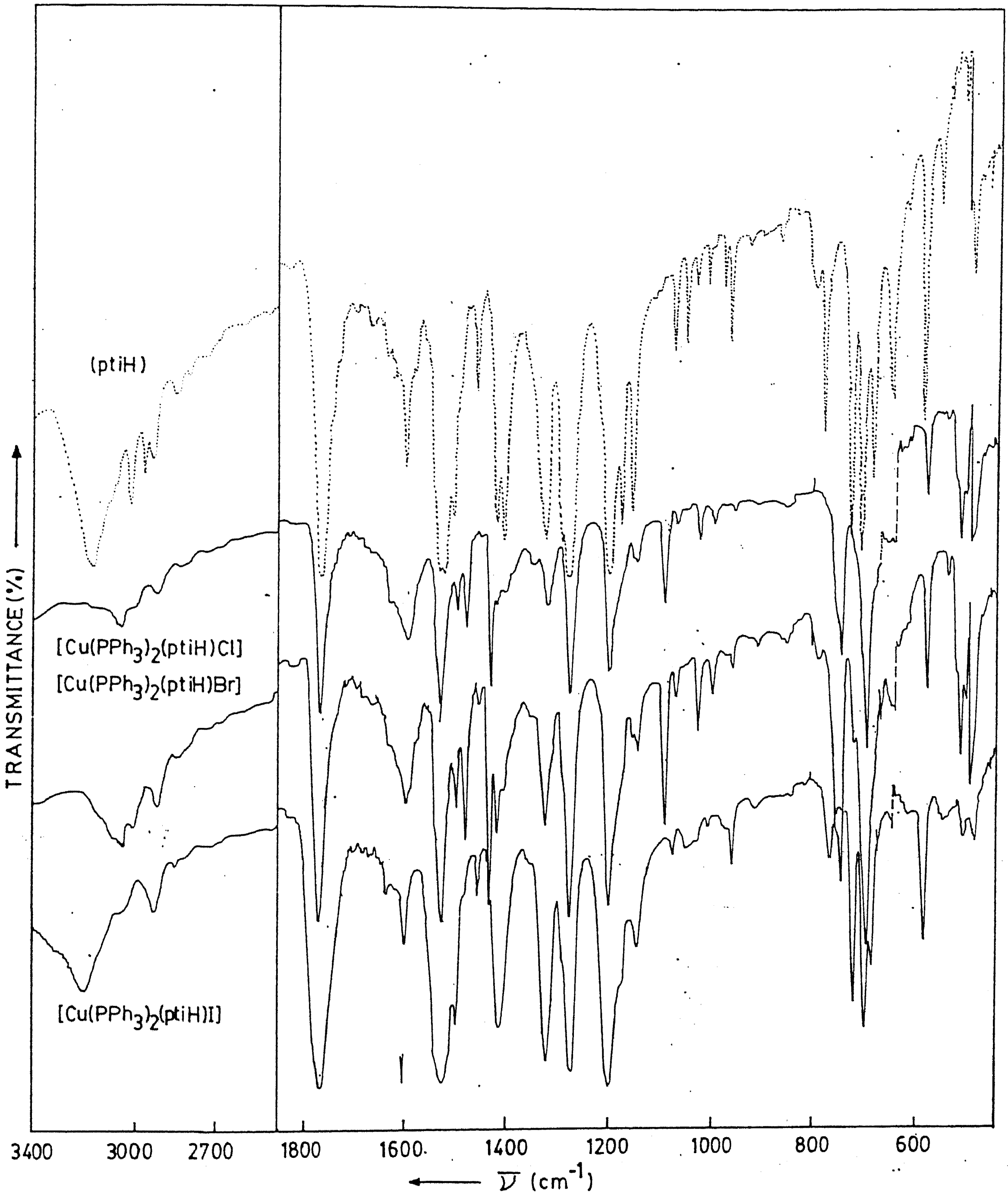


Figure 2.1. The IR spectra of the ligand ptiH and its complexes.

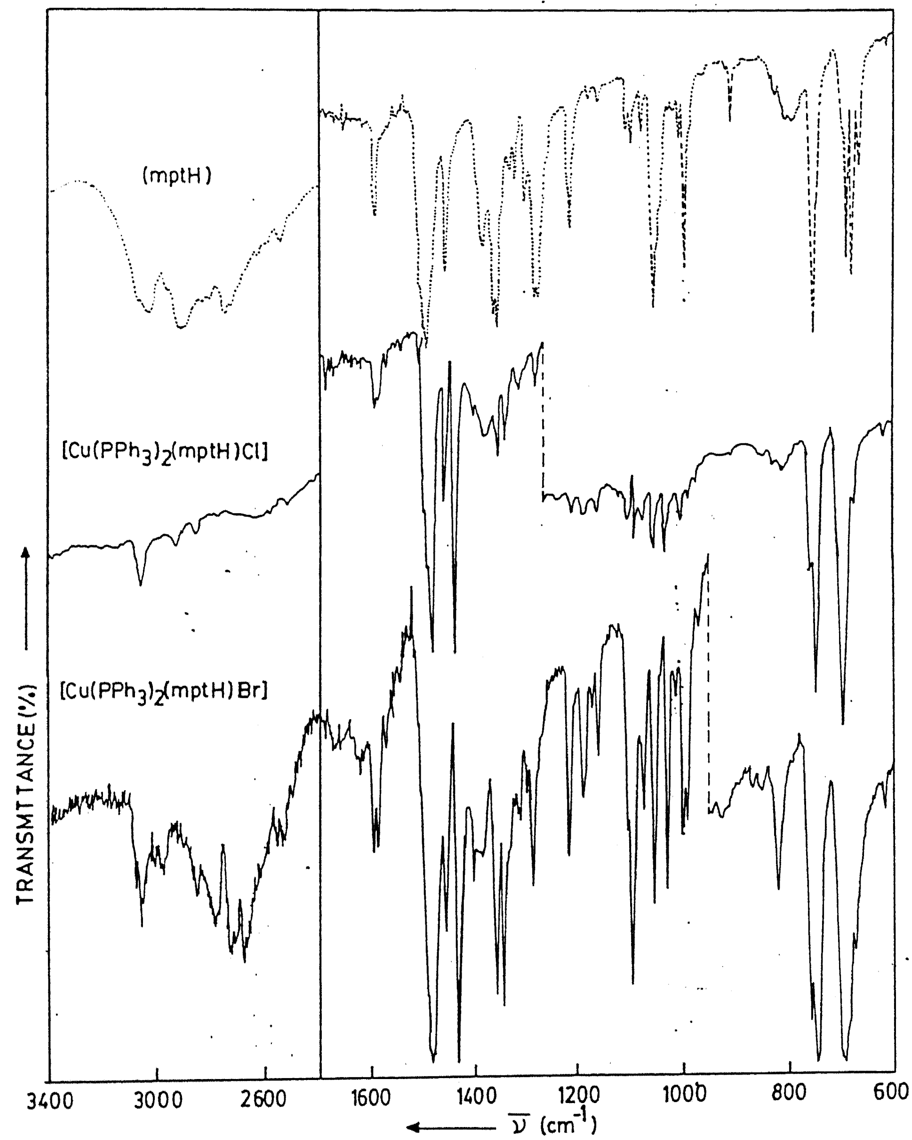


Figure 2.2. The IR spectra of the ligand mptH and its complexes.

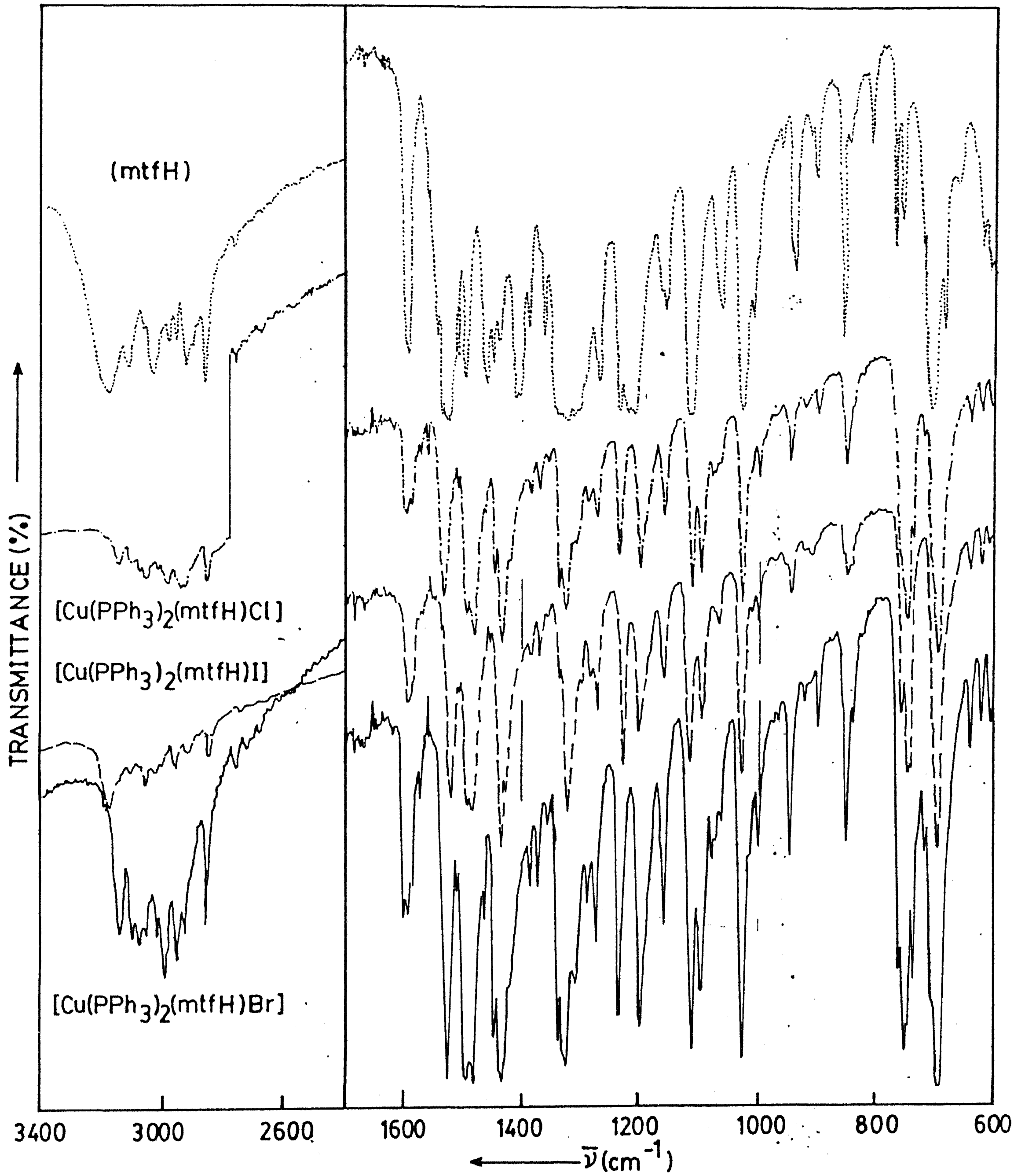


Figure 2.3. The IR spectra of the ligand mtfH and its complexes.

Table 2.2. Major IR bands of ligands and complexes (cm^{-1})

Compound	ν(NH)	ν(C=O)	ν(C=S)	Thioamide bands I	II	III	IV
Ligand (ptiH)	3180	1770	1165	1530	1300	1020	780
$[Cu(PPh_3)_2(ptiH)Cl]$	3170	1780	1150	1510	1290	1010	750
$[Cu(PPh_3)_2(ptiH)Br]$	3175	1780	1150	1490	1290	1010	760
$[Cu(PPh_3)_2(ptiH)I]$	3177	1780	1150	1510	1280	970	770
Ligand (mptH)	3023, 2904, 2745	----	1050	1492	1298	1002	751
$[Cu(PPh_3)_2(mptH)Cl]$	2940	----	1030	1480	1280	980	740
$[Cu(PPh_3)_2(mptH)Br]$	3054, 2782, 2681	----	1027	1485	1290	992	744
$[Cu(PPh_3)_2(mptH)I]$	2980, 2858, 2738	----	1027	1485	1295	997	745
Ligand (mtfH)	3174-2858	----	1118	1523-1536	1350-1350	1011	808
$[Cu(PPh_3)_2(mtfH)Cl]$	3141-2855	----	1095	1481	1287	999	744
$[Cu(PPh_3)_2(mtfH)Br]$	3135-2854	----	1095	1481	1286	999	759
$[Cu(PPh_3)_2(mtfH)I]$	3172-2851	----	1094	1486	1285	998	757

ligands contain a thioamide group (H—N—C=S) and give rise to four characteristic thioamide bands, namely, I, II, III, and IV, in the regions of 1500, 1300, 1000 and 800 cm^{-1} and have contributions from ν(C-N)+δ(N-H); ν(C=S)+ν(C=N)+ν(C-H); ν(C-N)+ν(C-S) and ν(C-S) modes of vibrations, respectively,[241-143] Figures 2.1, 2.2 and 2.3.

All complexes exhibit the characteristic IR bands of triphenylphosphine.[76,244] In the case of coordination of the ligand having a carbonyl group, namely ptiH, through the carbonyl oxygen atom, the ν(C=O) should shift to a lower wave number and the thioamide band I [δ(N-H)+ν(C-N)] should shift to a higher wave number. Whereas, if coordination is through the N atom, the thioamide band I will shift to a lower wave number. But the position of the band at *ca* 1770 cm^{-1}, assigned to ν(C=O), shifts towards higher wave number, Figure 2.1, (*ca* $\Delta\bar{\nu}$ = 10 cm^{-1}) in the complexes ruling out coordination through the carbonyl group. The band at *ca* 1165 cm^{-1}, assigned to ν(C=S) in the spectra of the ligands either splits or shifts to lower wave number (*ca* $\Delta\bar{\nu}$ = 15 cm^{-1}) on coordination. The thioamide band IV which contains a major contribution from ν(C—S) shifts by *ca* $\Delta\bar{\nu}$ = 10-15 cm^{-1} to lower wave number which may indicate the involvement of the C=S group in the coordination.

The band at 3180 cm^{-1} assigned to ν(N-H) for ptiH

becomes weak and broad in the IR spectra, Figure 2.1, of the complexes. The discernible ν(N-H) bands of the remaining ligands, Figure 2.2 and 2.3 (Table 2) shift only a little to lower region on complexation, indicating the non-involvement of the N-H group in the coordination. The lower shifting of ν(NH) may be due to hydrogen bonding.

Bonding via sulphur is also favoured in the complexes because copper(I), being a soft acid, should prefer to interact with a soft base such as sulphur and, indeed, the presence of a sulphur-copper(I) bond is confirmed by X-ray single crystal structure of many complexes of ligands having a thioamide group.[245,29,106,66]

2.3.2 Electronic (UV-vis) and ^{1}H NMR Spectra

The ^{1}H NMR spectra of some of the representative complexes and ligands, and the electronic (UV-vis) spectra of the complexes and free ligands are given in Figures 2.4, 2.5, 2.6 and Figures 2.7, 2.8, 2.9 respectively and the data are collected in Table 2.3 with assignments. As expected, only UV absorption bands are observed which are assigned as intra-ligand (IL) bands. The ^{1}H NMR spectra of the complexes clearly show the peaks due to ligands and PPh_3. The >NH proton signals are not observed in these complexes. It may be because of the hydrogen bonding in the complexes.

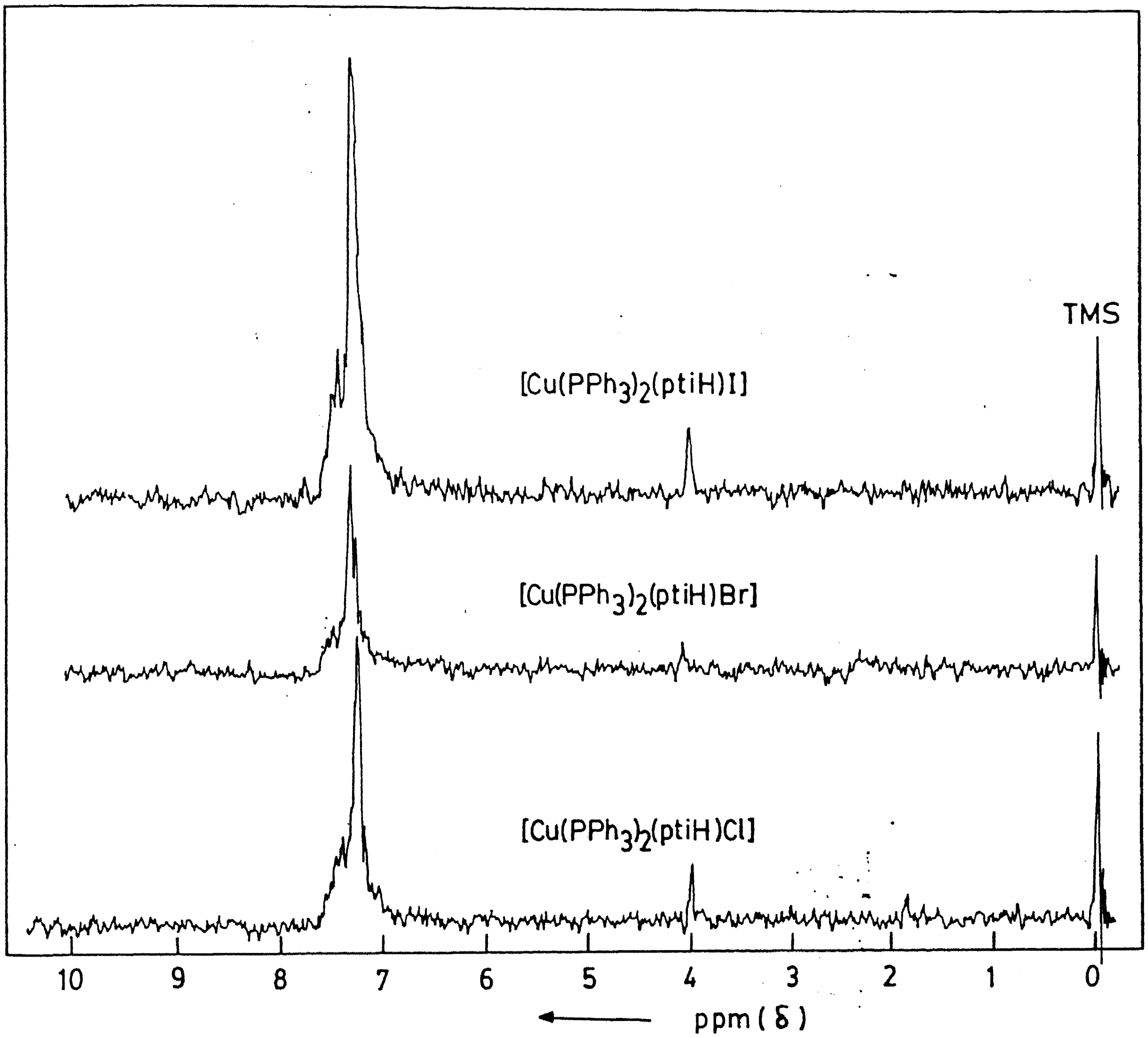


Figure 2.4. The ^{1}H NMR spectra of the complexes having ligand ptiH.

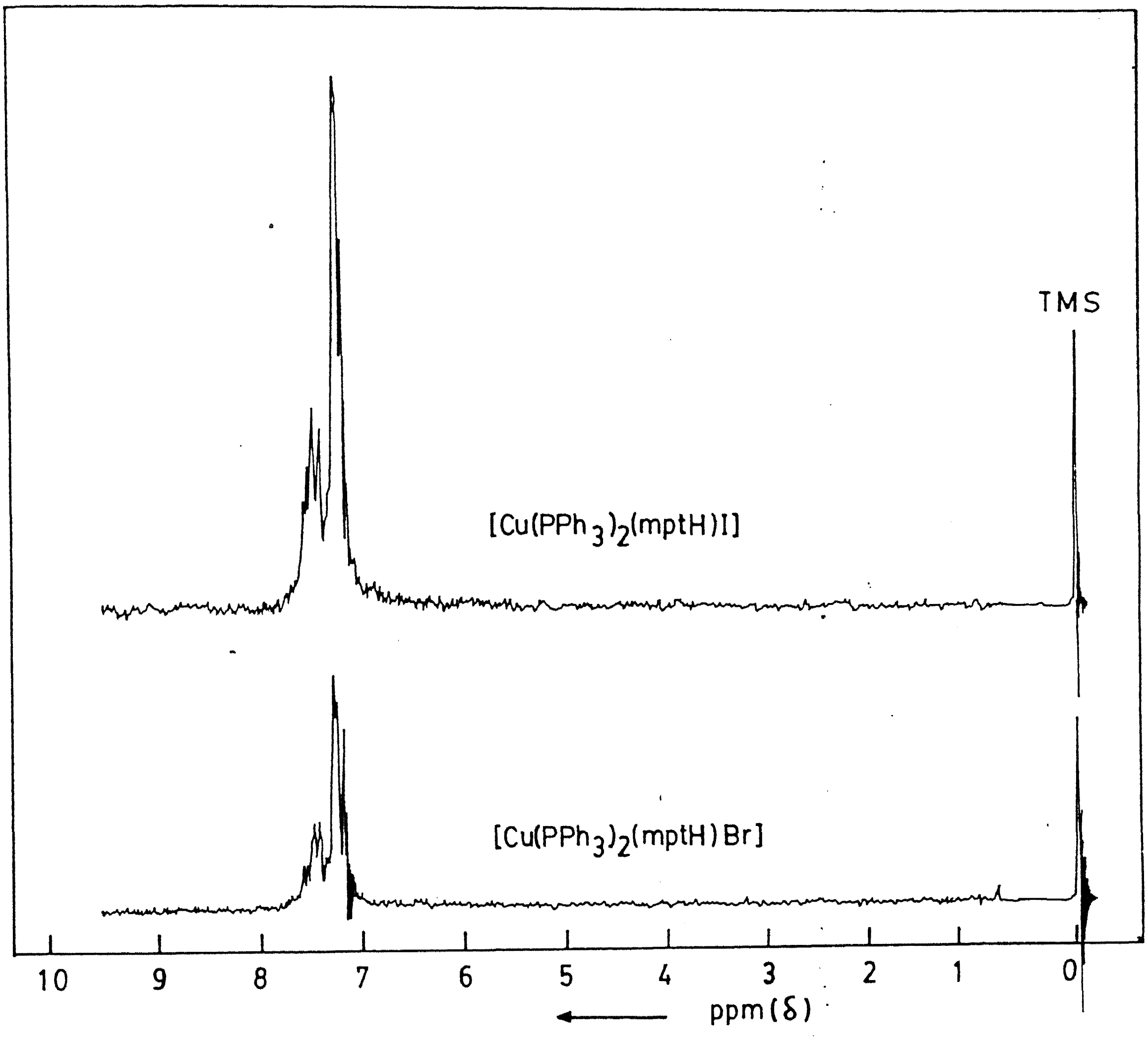


Figure 2.5. The ^{1}H NMR spectra of the complexes having ligand mptH.

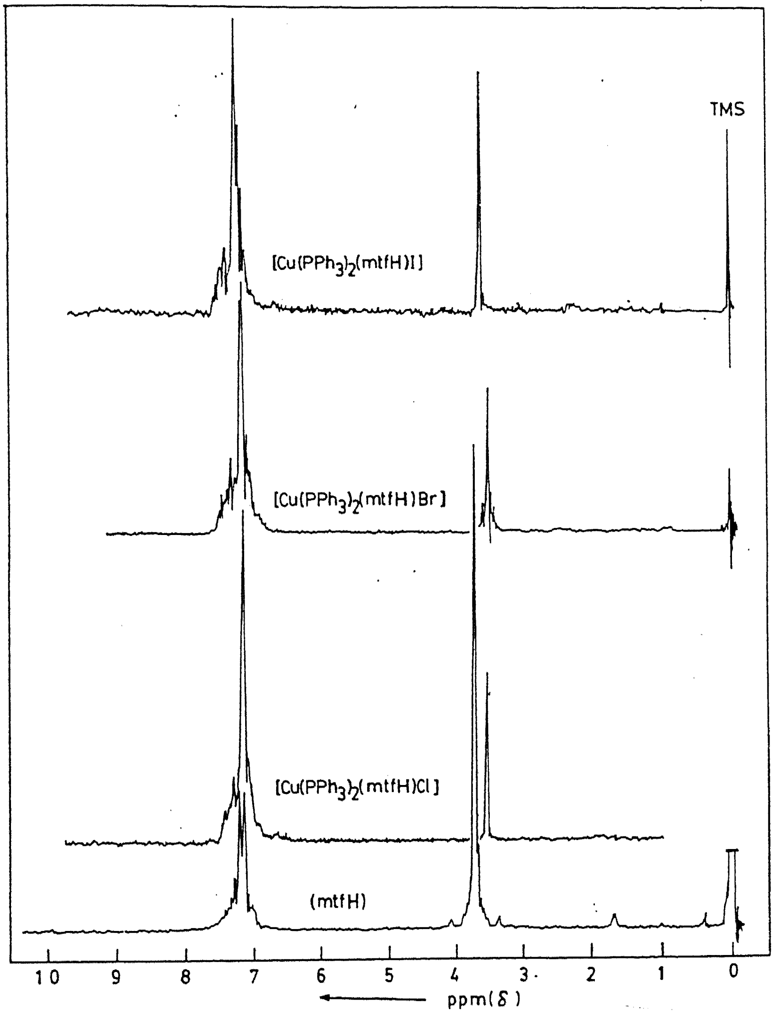


Figure 2.6. The ^{1}H NMR spectra of the ligand mtfH and its complexes.

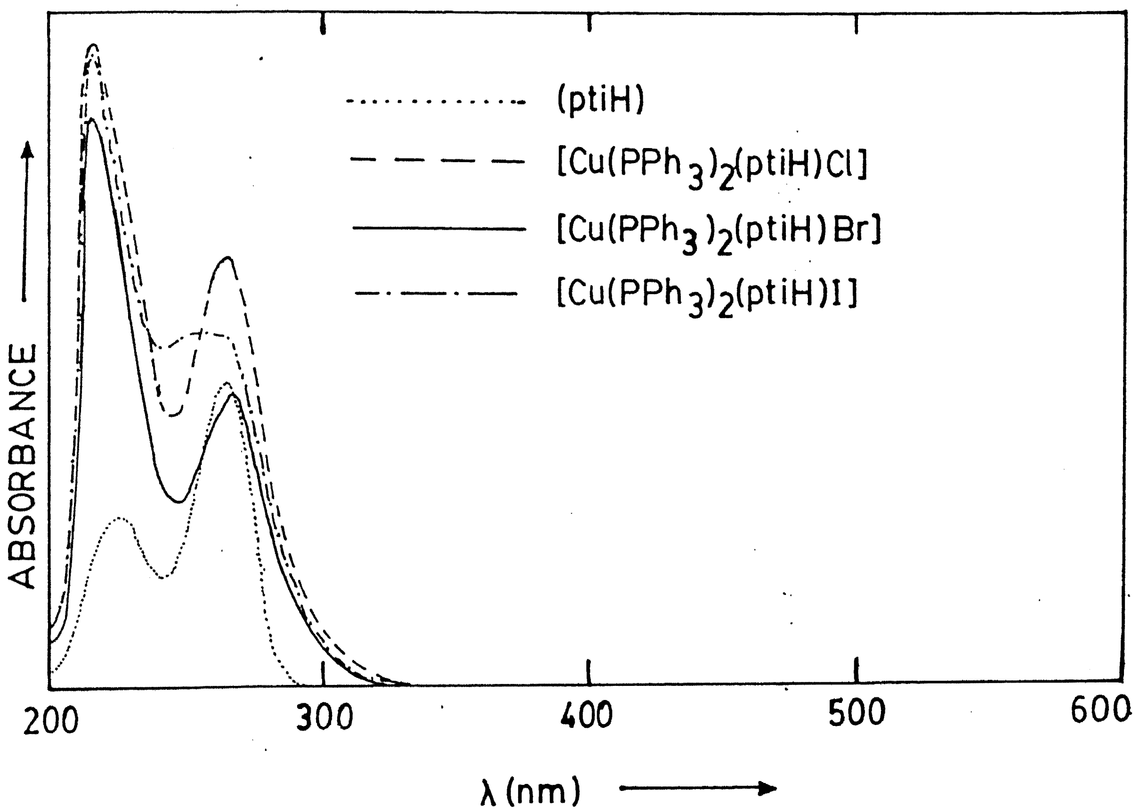


Figure 2.7. The electronic (UV-vis) spectra of the ligand ptiH and its complexes.

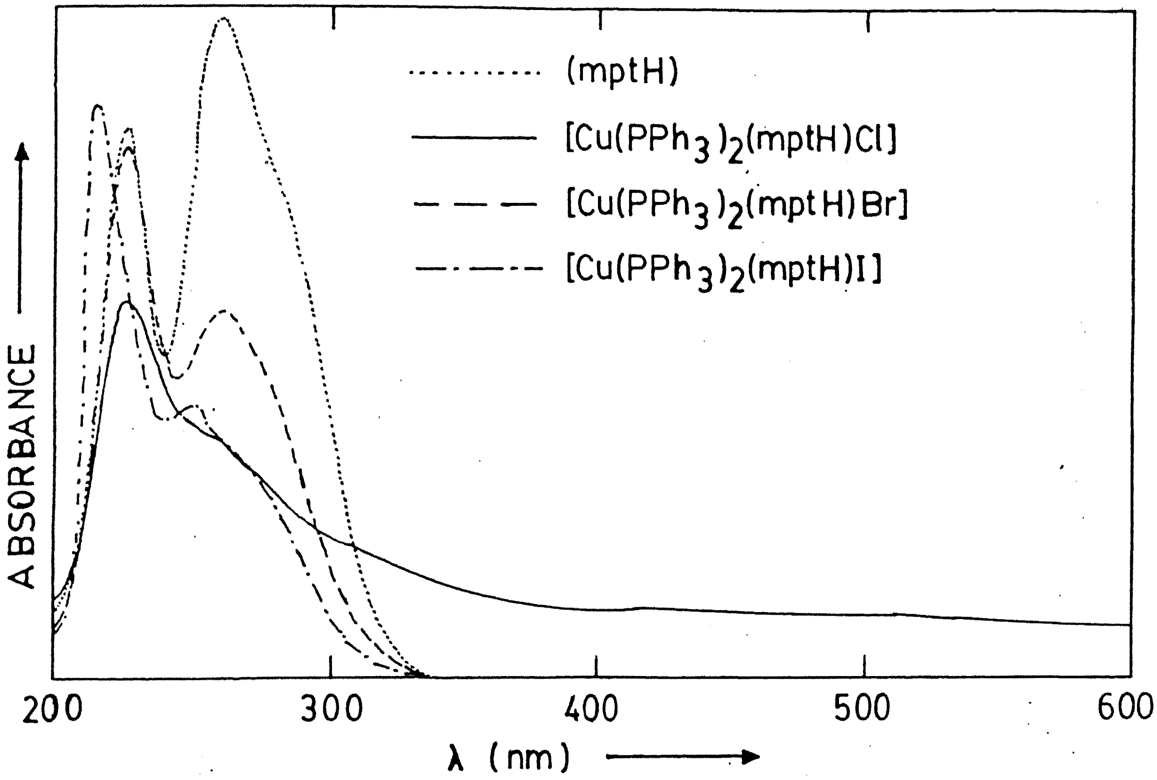


Figure 2.8. The electronic (UV-vis) spectra of the ligand mptH and its complexes.

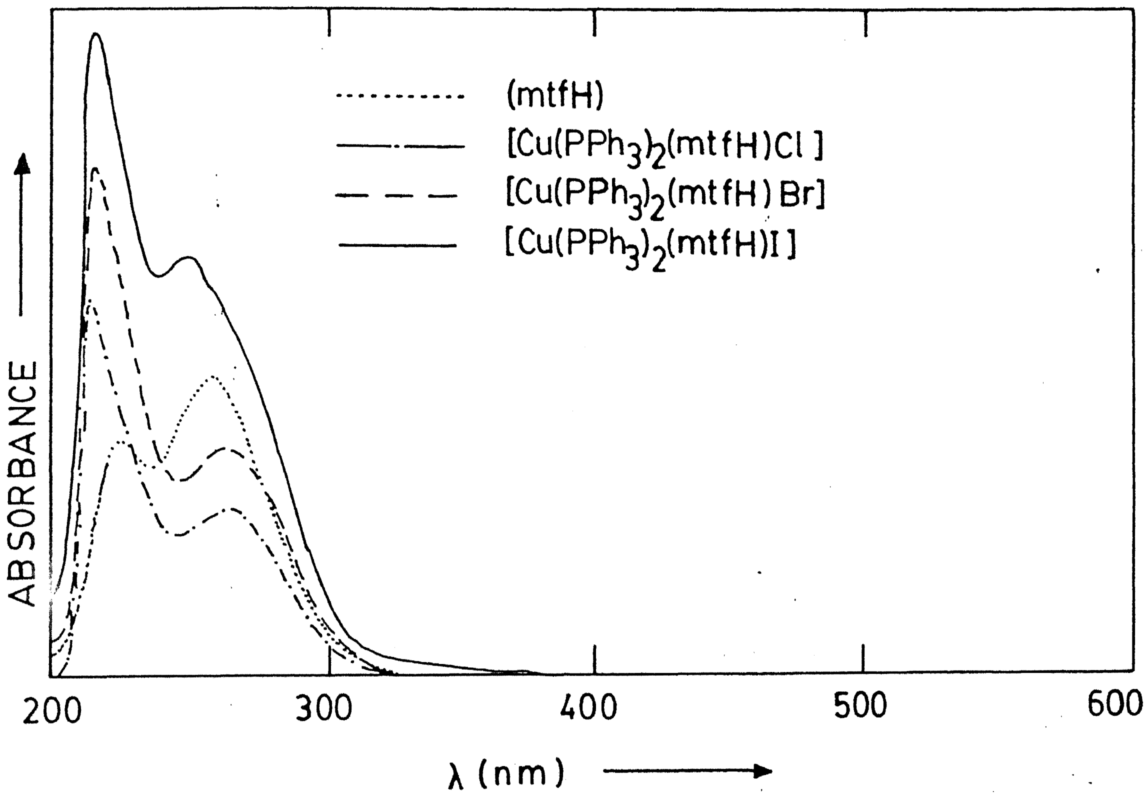


Figure 2.9. The electronic (UV-vis) spectra of the ligand ptfH and its complexes.

Table 2.3. Electronic (UV-vis) spectral data of the ligands and the complexes in CH_3CN, and ^1H NMR spectral data of the ligands and complexes in $CDCl_3$

Compound	Electronic (UV-vis) Band position, λ_{max}(nm), with Assignments	^1H NMR Signal with Assignments ppm(δ)
1	2	3
Ligand (ptiH)	227.0	4.30 (s, 2H, >CH_2 ring);
	265.0	7.28 (m, 3H, *ortho*-H of $-C_6H_5$); *ca* 7.46 (m, *meta*- and *para*-H of $-C_6H_5$); 10.37 (s, H, >NH group)[a]
$[Cu(PPh_3)_2(ptiH)Cl]$	216.0 IL	4.00 (s, 2H, >CH_2 ring);
	265.5 IL	6.83-7.67 (m, $-C_6H_5$ groups)
$[Cu(PPh_3)_2(ptiH)Br]$	216.0 IL	4.10 (s, 2H, >CH_2 ring);
	267.0 IL	7.00-7.67 (m, $-C_6H_5$ groups)
$[Cu(PPh_3)_2(ptiH)I]$	216.0 IL	4.00 (s, 2H, >CH_2 ring);
	262.5 IL	6.83-7.67 (m, $-C_6H_5$ groups)
Ligand (mptH)	227.0	7.63 (m, 3H, *ortho*- and *para*-H of
	259.5	$-C_6H_5$ groups); 7.89 (m, 2H, *meta*-H of $-C_6H_5$); 10.50-13.50 (s, H, -SH)[b]
$[Cu(PPh_3)_2(mptH)Cl]$	227.5 IL	6.83-7.67 (m, $-C_6H_5$ groups)
	259sh[c] IL	

Table 2.3. (contd...)

1	2	3
$[Cu(PPh_3)_2(mptH)Br]$	227.0 IL 261.0 IL	6.83-7.67 (m, $-C_6H_5$ groups)
$[Cu(PPh_3)_2(mptH)I]$	216.0 IL 252.0 IL	7.00-7.67 (m, $-C_6H_5$ groups)
Ligand (mtfH)	225.5 257.5	3.73 (s, 8H, $>CH_2$ groups of $-N\langle\ \rangle O$); 7.13 and 7.20 (d, 5H, $-C_6H_5$ group)[d]
$[Cu(PPh_3)_2(mtfH)Cl]$	214.5 IL 265.0 IL	3.57 (s, 8H, $>CH_2$ groups of $-N\langle\ \rangle O$); 6.83-7.50 (m, $-C_6H_5$ groups)
$[Cu(PPh_3)_2(mtfH)Br]$	216.0 IL 258.0 IL	3.57 (s, 8H, $>CH_2$ groups of $-N\langle\ \rangle O$); 6.83-7.50 (m, $-C_6H_5$ groups)
$[Cu(PPh_3)_2(mtfH)I]$	216.0 IL 257.0 IL	3.63 (s, 8H, $>CH_2$ groups of $-N\langle\ \rangle O$); 6.83-7.67 (m, $-C_6H_5$ groups)

[a]these are the literature values from ref. 235, in dmso-d_6; [b]these are the literature values from ref. 236, in dmso-d_6; [c]sh = shoulder; [d]literature values from ref. 237, are 3.74, 3.80 ppm(δ) and 7.15, 7.34 ppm(δ), peak due to NH hydrogen is not determined in this reference.

2.4 SUMMARY

Reactions of $[Cu(PPh_3)_3X]$ with the title ligands yield $[Cu(PPh_3)_2(LH)X]$. These complexes have been characterized on the basis of analyses, IR, electronic(UV-vis) and ^1H NMR spectral studies, conductivity and magnetic measurements. In all the cases there is a distorted tetrahedral environment around Cu(I) and the ligands (LH) bind through the thione sulphur atom to copper(I).

CHAPTER 3*

SYNTHESIS AND CHARACTERIZATION OF $[Cu(AsPh_3)_2(LH)X]$ (LH = ptiH, mptH; X = Cl, Br, I)

3.1 INTRODUCTION

The study of the coordination of $AsPh_3$ to copper(I) centre seems interesting since the arsine ligand is softer than the corresponding phosphine, almost equally bulky and has been found to express interesting features upon coordination to copper(I).[246,247] The arsine complexes $[Cu(tclH)_2(AsPh_3)X]$,[68] (X = Cl, Br, I) have been reported to exhibit a remarkable photostability compared to their phosphine counterparts. Moreover, they do not react with stoichiometric amounts of pyridine which, in the case of phosphine complexes displaces the thione ligands coordinated to copper. Such glaring differences prompted us to study the triphenylarsine analogues of the complexes described in

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* R. Singh and S. K. Dikshit, *Polyhedron*, **1993**, *12*, 759.

chapter 2. With this objective, the synthesis and characterization of a new series of mixed ligand compounds with Cu—As bonds are presented in this chapter.

3.2 EXPERIMENTAL

3.2.1 Starting Materials

All the chemicals used are either of Analar or chemically pure grade. The ligands 3-phenyl-2-thioxoimidazolidin-4-one (ptiH); and 5-mercapto-1-phenyl-1,2,3,4-tetrazole (mptH) have been prepared by the methods described in previous chapter. The complexes of the type $[Cu(AsPh_3)_3X]$,[61] (X = Cl, Br or I) have been synthesized by the literature methods with a minor modification. A brief description of the method is as given below:

3.2.1(a) Preparation of $[Cu(AsPh_3)_3X]$ (X = Cl, Br, I)

Refluxing of 1:4 molar quantity of CuX and $AsPh_3$ in benzene produces a clear solution and it is left for cooling and after slow evaporation of the solvent the crystalline complexes are obtained which are collected by filtration and washed with ether.

3.2.2 Physical Methods

These are same as described in the previous chapter.

3.2.3 Preparation of Compounds

3.2.3(a) Preparation of $[Cu(AsPh_3)_2(ptiH)X]$

To a benzene solution (30 mL) of air stable compound $[Cu(AsPh_3)_3X]$ (0.2 mmol), an equivalent amount (0.2 mmol) of the ligand ptiH, is added and the solution/suspension is heated under reflux for about 2 hours. During refluxing, the reaction mixture becomes almost clear. After cooling, the solution is filtered through a Whatman No. 1 filter paper to remove any insoluble particles. The resulting solution is concentrated under reduced pressure to half of its volume. Addition of petroleum ether (60-80°C) (50 mL) results in the precipitation of the microcrystalline products on standing for 2-3 hours. The complexes are centrifuged and washed several times with petroleum ether and dried *in vacuo*.

3.2.3(b) Preparation of $[Cu(AsPh_3)_2(mptH)X]$

To a benzene solution (30 mL) of $[Cu(AsPh_3)_3X]$ (0.2 mmol), an equivalent amount (0.2 mmol) of the ligand mptH, is added and the resulting clear solution is stirred for about 3 hours. During stirring some crystals of the complexes appear. The volume of the reaction mixture is reduced to about 5 mL

under vacuum and excess petroleum ether (60-80°C) (50 mL) is added to ensure the maximum precipitation of the complexes. These complexes are centrifuged and washed several times with petroleum ether and dried *in vacuo*.

All these compounds are stable in air for several days but a few complexes are susceptible to air oxidation when left in air for more than a week. The air oxidized products have not been further studied. Melting point, yield and colour of the complexes are given in Table 3.1 along with the analytical data.

3.3 RESULTS AND DISCUSSION

Analytical data are in good agreement with the stoichiometry proposed as $[Cu(AsPh_3)_2(LH)X]$, Table 3.1. These compounds are soluble in most of the organic solvents like C_6H_6, $CHCl_3$, CH_2Cl_2, DMSO, DMF, CH_3CN etc. All the compounds are diamagnetic at room temperature. The conductivity of the complexes is in the range of 50 to 65 $ohm^{-1}cm^2mol^{-1}$ in acetonitrile and, consequently, are interpreted according to Geary[240] as being non electrolytes.

3.3.1 IR Spectra

IR spectra of the ligands and complexes are given in Figures 3.1 and 3.2, and the data are summarized in Table 3.2. All the ligands adopt the thione form both in the free

Table 3.1 Analytical data of the complexes with colour, melting point (M. p.) and yield

Compound	Colour	Analytical data, Found (Calculated) (%) C	H	N	Cu	S	Halide	M. p.[a] (θ/°C)	Yield (%)
(1) $[Cu(AsPh_3)_2(ptiH)Cl]$	Maroon	54.5 (54.3)	3.6 (3.9)	4.6 (4.7)	10.8 (10.6)	5.3 (5.4)	6.0 (5.9)	95d	82
(2) $[Cu(AsPh_3)_2(ptiH)Br]$	White	50.6 (50.5)	3.5 (3.6)	4.2 (4.4)	9.7 (9.9)	5.2 (5.0)	12.3 (12.5)	140d	85
(3) $[Cu(AsPh_3)_2(ptiH)I]$	White	47.2 (47.1)	3.3 (3.4)	4.2 (4.1)	9.5 (9.2)	4.9 (4.7)	18.6 (18.4)	135d	80
(4) $[Cu(AsPh_3)_2(mptH)Cl]$	White	51.2 (51.5)	3.7 (3.6)	9.9 (9.6)	10.7 (10.9)	5.3 (5.5)	5.9 (6.1)	158d	45
(5) $[Cu(AsPh_3)_2(mptH)Br]$	White	47.2 (47.8)	3.2 (3.4)	8.7 (8.9)	10.3 (10.1)	5.3 (5.1)	12.9 (12.7)	158d	58
(6) $[Cu(AsPh_3)_2(mptH)I]$	Orange	44.3 (44.5)	3.2 (3.1)	8.6 (8.3)	9.6 (9.4)	4.8 (4.8)	18.7 (18.8)	160d	46

[a]d = decomposed

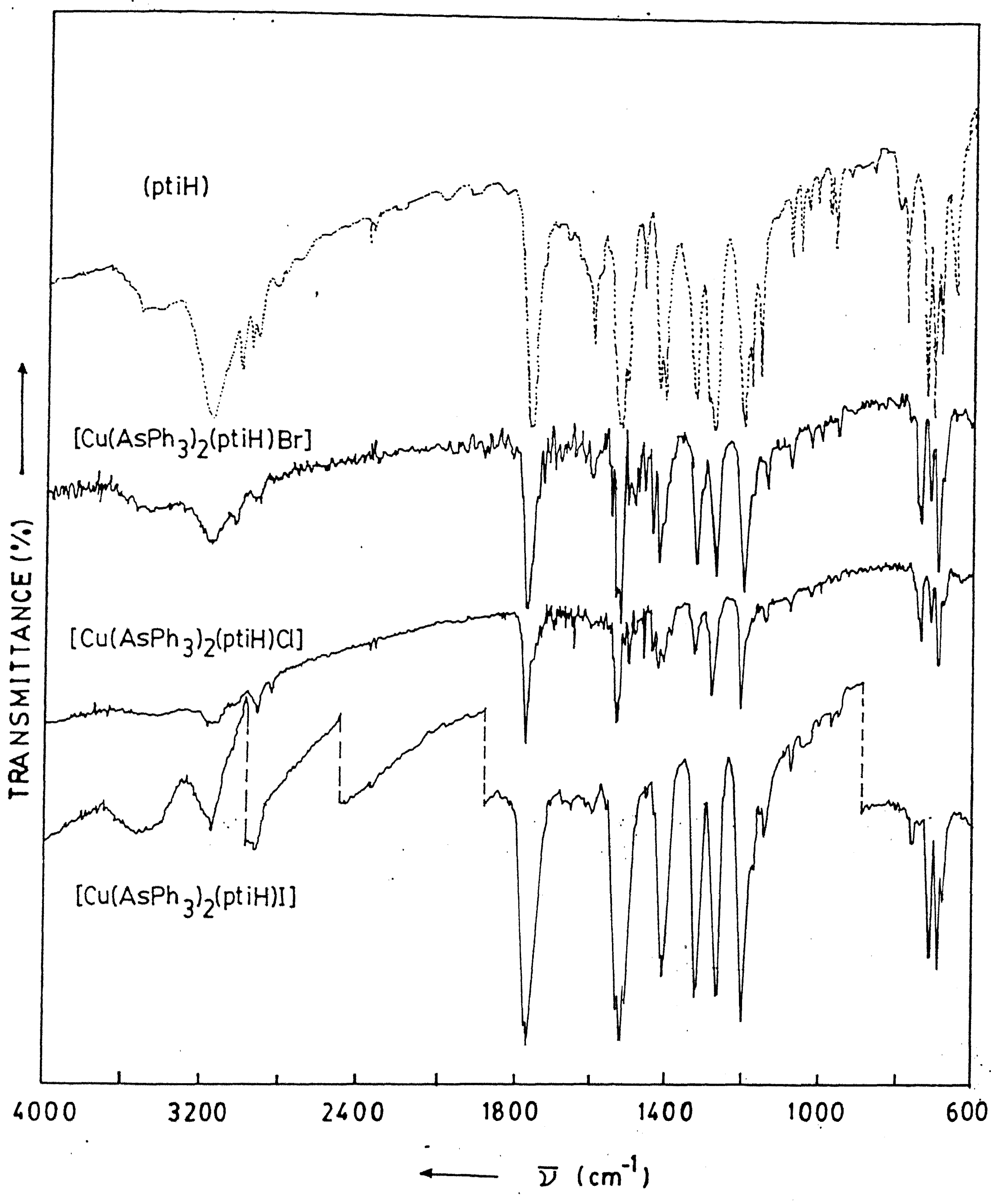

Figure 3.1. The IR spectra of the ligand ptiH and its complexes.

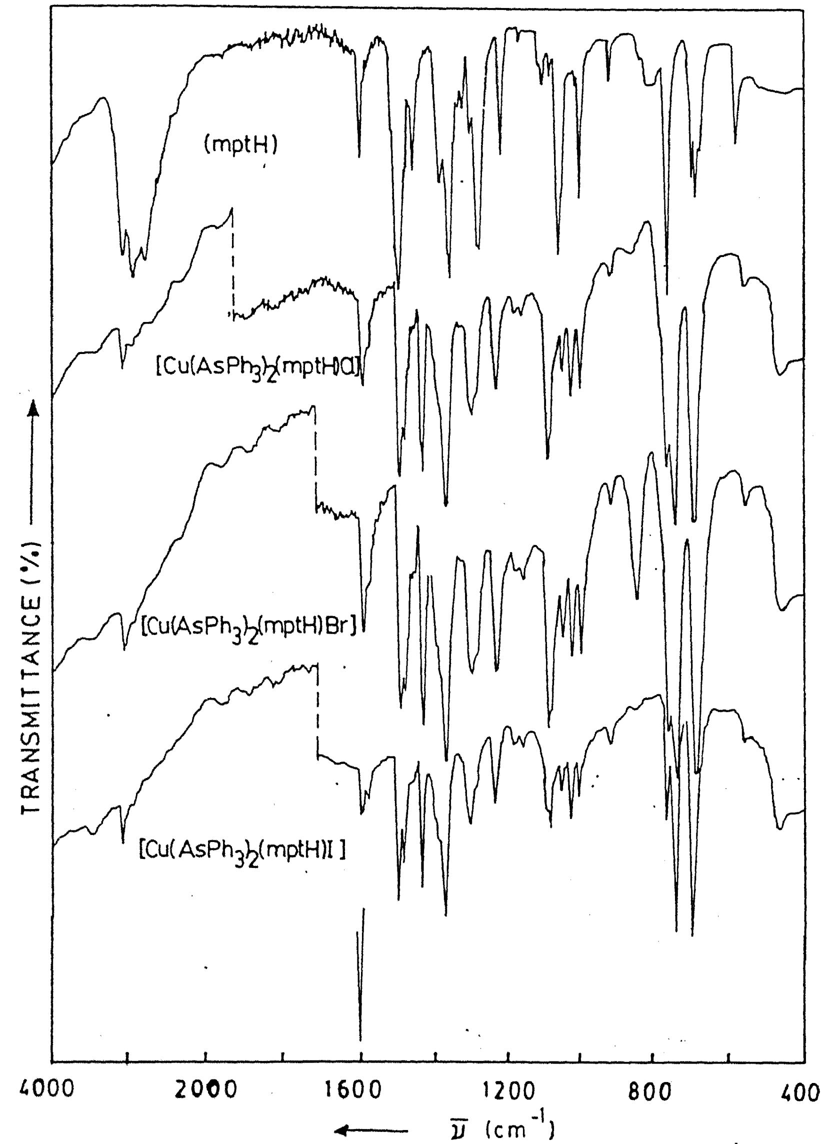

Figure 3.2. The IR spectra of the ligand mptH and its complexes.

Table 3.2 Major IR bands of the ligands ptiH, mptH and their complexes (cm^{-1})

Compound	ν(NH)	ν(C=O)	ν(C=S)	Thioamide Bands I	II	III	IV
Ligand (ptiH)	3180	1770	1165	1530	1300	1020	780
[$Cu(AsPh_3)_2$(ptiH)Cl]	3177	1771	1080	1532	1324	1140	745sh
[$Cu(AsPh_3)_2$(ptiH)Br]	3180	1776	1077	1530	1320	1139	746sh
[$Cu(AsPh_3)_2$(ptiH)I]	3240	1775	1075	1525	1320	1145	760
Ligand (mptH)	3023	----	1050	1492	1279	1002	751
	2904				1298	993	793
[$Cu(AsPh_3)_2$(mptH)Cl]	2900	----	1040	1495	1300	995	754
[$Cu(AsPh_3)_2$(mptH)Br]	2900	----	1045	1495	1300	995	752
[$Cu(AsPh_3)_2$(mptH)I]	2950	----	1050	1505	1310	1000	751

sh = shoulder

state and in their complexes. This is evident by the absence of the ν(SH) band in the region of 2500 cm^{-1}, and by the presence of ν(NH) in the region[228] of 2900 to 3300 cm^{-1}. The ligands contain a thioamide group (H—N—C=S) and give rise to four characteristic thioamide bands, namely, I, II, III, and IV, in the regions of 1500, 1300, 1000 and 800 cm^{-1} and have contributions from ν(C-N)+δ(N-H); ν(C=S)+ν(C=N)+ν(C-H); ν(C-N)+ν(C-S) and ν(C-S) modes of vibrations, respectively,[227,241-243] Figures 3.1 and 3.2.

All complexes exhibit the characteristic bands of triphenylarsine.[76] In the case of coordination of the ligand having a carbonyl group, namely ptiH, through the carbonyl oxygen atom, the ν(C=O) should shift to a lower wave number and the thioamide band I [ν(C-N)+δ(N-H)] should shift to a higher wave number. Whereas, if coordination is through the nitrogen atom, the thioamide band I will shift to a lower wave number. But the position of the band at *ca* 1770 cm^{-1}, assigned to ν(C=O), remains almost unaffected or slightly shifts to the higher wave number (*ca* $\Delta\bar{\nu}$ = 1-6 cm^{-1}) in the complexes ruling out coordination through the carbonyl group, Figure 3.1. The band at *ca* 1165 cm^{-1}, assigned to ν(C=S) in the spectra of the ligand ptiH, either splits or shifts to lower wave number (*ca* $\Delta\bar{\nu}$ = 10-15 cm^{-1}) on coordination. The thioamide band IV which contains a major contribution from

ν(C-S) splits or shifts to the lower region by *ca* $\Delta\bar{\nu}$ = 41-42 cm^{-1} which indicates the involvement of the C=S group in the coordination, Figure 3.1.

On complexation, the ν(C=S) of the ligand mptH at 1050 cm^{-1} splits, Figure 3.2. The thioamide band I at 1492 cm^{-1} undergoes blue shift by 3-16 cm^{-1}. The thioamide band IV at 793 cm^{-1} undergoes red shift (lit.[230] value 785 cm^{-1}), Figure 3.2. These observations support the bond formation between metal and thione sulphur.

The band at 3180 cm^{-1} assigned to ν(N-H) for the ligand ptiH becomes weak in the IR spectra of the complexes. The discernible ν(N-H) bands of the ligand mptH, Figure 3.2, shift little on complexation, indicating the noninvolvement of the N-H group in the coordination.

Bonding via sulphur is also favoured in the complexes because copper(I), being a soft acid, should prefer to interact with a soft base such as sulphur and, indeed, the presence of a sulphur-copper(I) bond is confirmed by X-ray single crystal structure of many complexes having a heterocyclic thione ligand possessing an α-nitrogen heteroatom.[248,29,70,65] Very recently the mixed ligand coordination compounds of copper(I) with heterocyclic thiones and triphenylarsine[249] have been synthesized and their X-ray crystal structural characterization has been done in which

exactly same type of coordination environment and stoichiometry have been observed.

3.3.2 Electronic (UV-vis) and ^{1}H NMR Spectra

The ^{1}H NMR spectra of the complexes (2), (3) and the electronic (UV-vis) spectra of the complexes and free ligands are given in Figure 3.3 and Figures 3.4, 3.5 respectively and the data are collected in Table 3.3 with assignments. The ^{1}H NMR spectra of the complexes clearly show the peaks due to the ligands and triphenylarsine. The ^{1}H NMR signal of the >NH proton of the complexes appear as broad signal. The broadening of the signals may be due to hydrogen bonding.[29,73,68] The δ values become lower as the halogen atomic radius increases (10.27 and 9.47 ppm(δ) in the bromine and iodine complexes of the ligand ptiH respectively).[68] The proportions of the protons, observed by integration, are matching with the proposed stoichiometry of the complexes. As expected, only UV absorption bands are observed which are assigned as intraligand (IL) transitions, Figure 3.4 and 3.5.

3.4 SUMMARY

Reactions of $[Cu(AsPh_3)_3X]$ with the title ligands yield $[Cu(AsPh_3)_2(LH)X]$. These complexes have been characterized on the basis of analytical, IR, electronic (UV-vis), ^{1}H NMR, conductivity and magnetic measurements. In all cases there is a distorted tetrahedral environment around Cu(I), and the

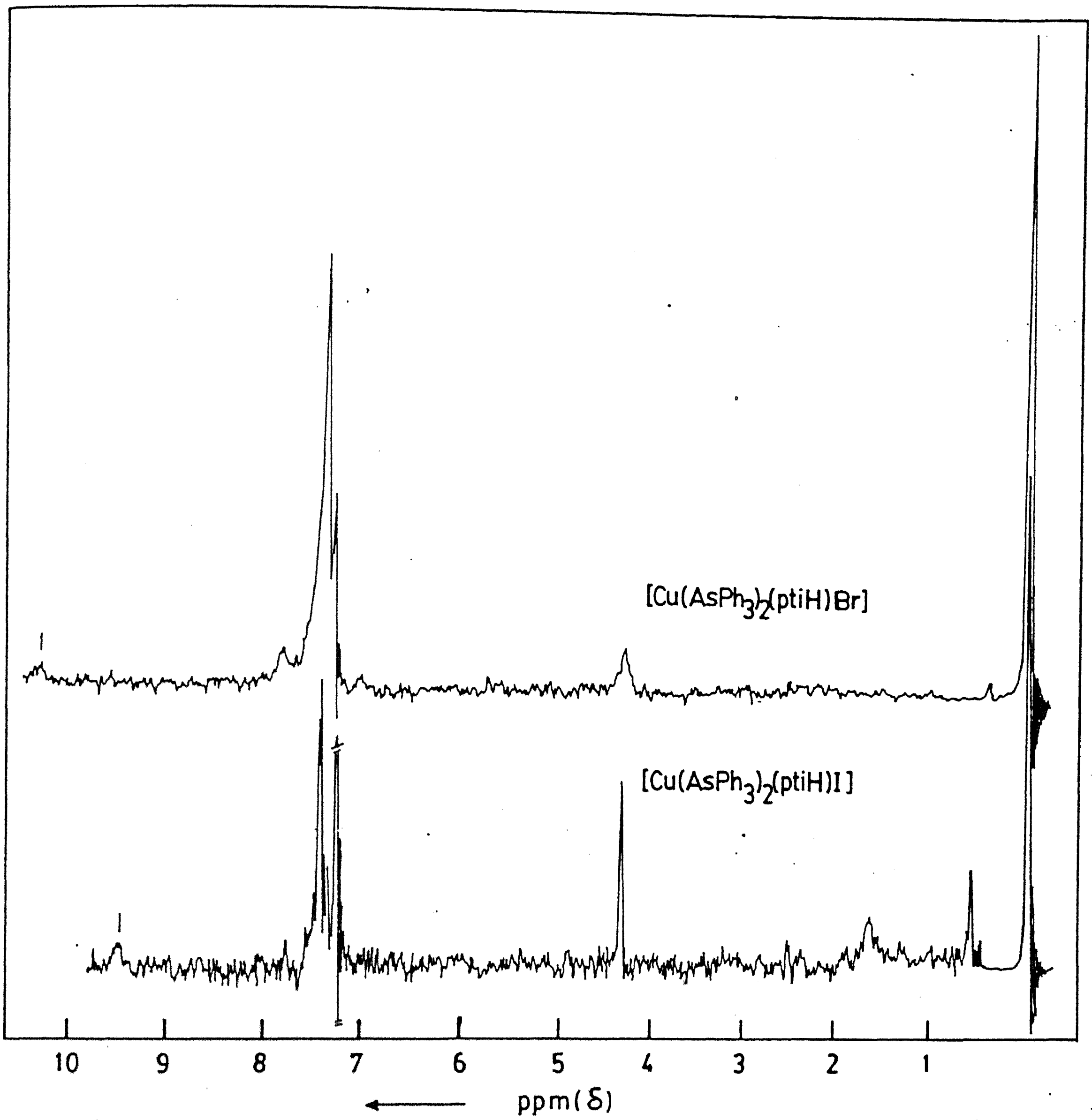

Figure 3.3. The ^{1}H NMR spectra of the complexes containing ligand ptiH.

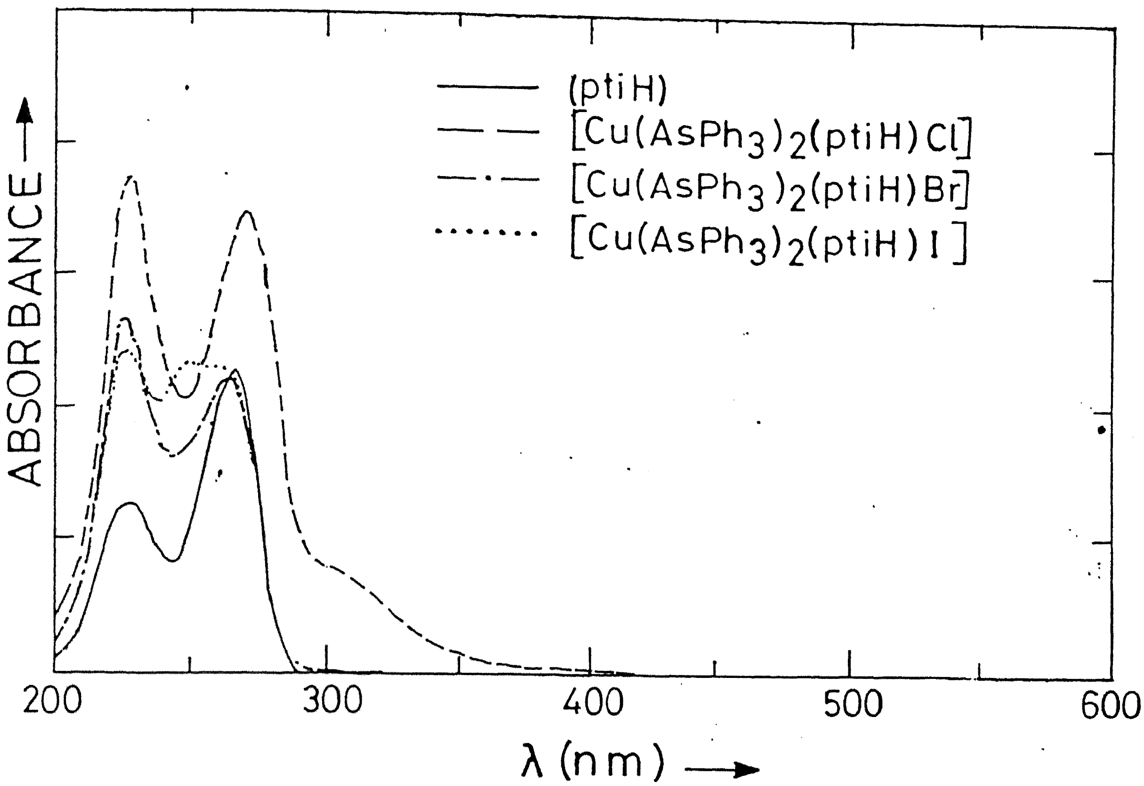

Figure 3.4. The electronic (UV-vis) spectra of the ligand ptiH and its complexes.

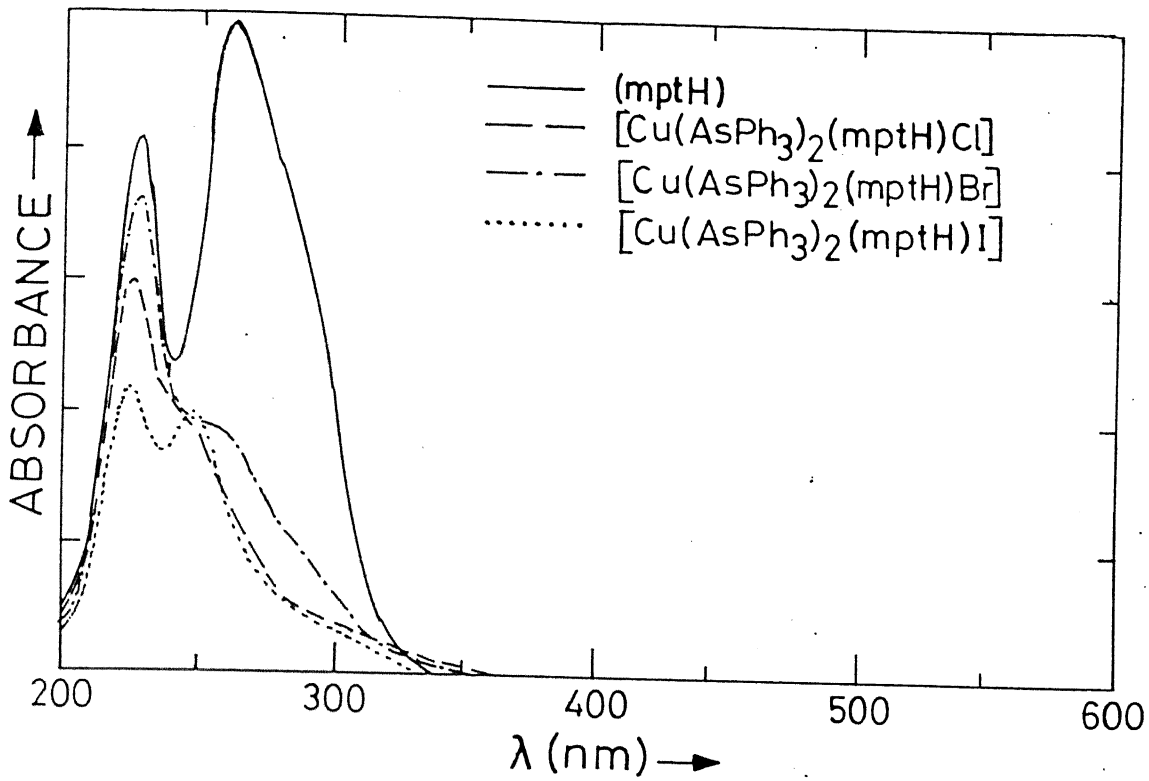

Figure 3.5. The electronic (UV-vis) spectra of the ligand mptH and its complexes.

Table 3.3. Electronic (UV-vis) spectral data of the ligands and their complexes in CH_3CN and ^1H NMR spectral data of the ligands and the complexes in $CDCl_3$

Compound	Band position, λ_{max}(nm), with Assignment		^1H NMR Signal with Assignments ppm(δ)
1	2		3
Ligand (ptiH)	227.0		4.30 (s, 2H, $>CH_2$ ring);
	265.0		7.28 (m, 3H, *ortho*-H of $-C_6H_5$); *ca* 7.46 (m, *meta*- and *para*-H of $-C_6H_5$); 10.37 (s, H, >NH group)[a]
$[Cu(AsPh_3)_2(ptiH)Cl]$	226.5	IL	4.00 (s, 2H, $>CH_2$ ring);
	270.0	IL	6.83-7.67 (m, 35H, $-C_6H_5$ groups)
	305.0sh	IL	
$[Cu(AsPh_3)_2(ptiH)Br]$	225.0	IL	4.10 (s, 2H, $>CH_2$ ring);
	263.0	IL	7.00-7.67 (m, 35H, $-C_6H_5$ groups); 10.27 [s(broad), 1H, >NH group]
$[Cu(AsPh_3)_2(ptiH)I]$	225.0	IL	4.00 (s, 2H, $>CH_2$ ring);
	249.5	IL	6.83-7.67 (m, 35H, $-C_6H_5$ groups) 9.47 [s(broad), 1H, >NH group]

Table 3.3. (contd...)

1	2		3
Ligand (mptH)	227.0		7.63 (m, 3H, *ortho*- and *para*-H
	259.5		of $-C_6H_5$ groups); 7.89 (m, 2H,
			meta-H of $-C_6H_5$)
			10.50-13.50 (s, 1H, -SH)[b]
$[Cu(AsPh_3)_2(mptH)Cl]$	225.0	IL	6.83-7.67 (m, $-C_6H_5$ groups)
	245.0sh	IL	
$[Cu(AsPh_3)_2(mptH)Br]$	226.5	IL	6.83-7.67 (m, $-C_6H_5$ groups)
	251.5	IL	
$[Cu(AsPh_3)_2(mptH)I]$	224.0	IL	7.00-7.67 (m, 35H, $-C_6H_5$ groups)
	247.0	IL	9.37 [s(broad), 1H, >NH group]

[a]these are the literature values from ref. 235, in dmso-d_6; [b]these are the literature values from ref. 236, in dmso-d_6; sh = shoulder.

ligands (LH) bind through the thione sulphur atom to copper(I).

CHAPTER 4*

SYNTHESIS AND CHARACTERIZATION OF $[Cu(PPh_3)_2(LH)X]$

(LH = DMPTH, DBPTH, TZDTH; X = Cl, Br, I)

4.1 INTRODUCTION

It is well known that the stoichiometry and geometry of the copper(I) complexes depends mostly on the electronic properties and bulk of the ligands around the metal centre. In the second chapter, the copper(I) complexes of some of the thione donor ligands and triphenylphosphine are described. In this chapter the mixed ligand complexes of copper(I) with triphenylphosphine and the thione ligands other than described in chapter 2 have been synthesized and characterized to study the effects on stoichiometry and geometry on varying the thione ligands.

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* R. Singh and S. K. Dikshit, *Polyhedron* **1992**, *11*, 2099.

4.2 EXPERIMENTAL

4.2.1 Starting Materials

All the chemicals used are either of Analar or chemically pure grade. The complexes of the type $[Cu(PPh_3)_3X]$ (X = Cl, Br, I), are prepared by the methods as briefly described in chapter 2. The ligands N,N-Dimethyl-N'-phenylthiourea (dmptH) and N,N-Dibutyl-N'-phenylthiourea (dbptH) are prepared by the direct addition of phenyl isothiocyanate to the appropriate secondary amine in methanol in 1:1 ratio and recrystallization of the product using acetone as solvent.[78] The ligand 1,3-thiazolidine-2-thione has been purchased from Eastern Organic Chemicals and it has been recrystallized from hot water before use.

4.2.2 Physical Methods

Elemental analyses, electronic (UV-vis) and ^{1}H NMR spectra and the magnetic, conductivity and melting point measurements are performed following the same procedure described in chapter 2, but the solvent for conductivity measurements are nitrobenzene. The IR spectra are recorded in KBr pellet in the range 4000-400 cm^{-1} on a Shimadzu IR-420 double beam spectrophotometer. The ^{31}P NMR (decoupled) are recorded on Varian Associates XL-300 FT-NMR Spectrometer using 85% H_3PO_4 as external calibrant. The ^{13}C NMR

(decoupled) are recorded on Varian Associates XL-200 FT-NMR spectrometer and peaks are relative to TMS (0 ppm).

4.2.3 Preparation of Compounds

In the benzene solution (50 mL) of $[Cu(PPh_3)_3X]$ (1 mmol) of the solution of equivalent amount of ligand (1 mmol) in benzene (25 mL) is added slowly and the clear mixture is heated under reflux for about 2 h. The resulting clear solution is concentrated to about 20 mL under reduced pressure. Addition of petroleum ether (60-80°C) (50 mL) and allowing to stand for 2-3 hours with occasional stirring yields the microcrystalline products. These complexes are centrifuged and washed several times with petroleum ether and dried *in vaccuo*. M. p., colour and yield of the complexes are given in Table 4.1 along with the analytical data.

4.3 RESULTS AND DISCUSSION

Analytical data of the complexes are given in Table 4.1 which are consistent with the stoichiometries proposed. Conductivity of the complexes is found to be in the range of 0.25 to 0.50 $ohm^{-1}cm^{-2}mol^{-1}$ in nitrobenzene solution indicating non-electrolytic nature of the complexes.[240] All complexes are diamagnetic at room temperature.

4.3.1 IR Spectra

IR spectra of the ligands dmptH, dbptH and their

Table 4.1. Analytical data of the complexes with colour, melting point (M. p.) and yield.

Compound (colour)	Analytical data Found (Calculated) (%) C	H	N	Cu	S	Halide	M.p. (θ/°C)	Yield (%)
(1) $[Cu(PPh_3)_2(dmptH)Cl]$ (White)	67.26 (67.31)	5.19 (5.27)	3.51 (3.49)	7.63 (7.90)	3.90 (3.99)	4.45 (4.42)	169	89
(2) $[Cu(PPh_3)_2(dmptH)Br]$ (White)	63.70 (63.78)	5.03 (5.00)	3.28 (3.31)	7.51 (7.50)	3.80 (3.78)	9.42 (9.40)	168	86
(3) $[Cu(PPh_3)_2(dmptH)I]$ (White)	60.45 (60.43)	4.71 (4.73)	3.15 (3.13)	7.13 (7.10)	3.56 (3.58)	14.18 (14.19)	161	98
(4) $[Cu(PPh_3)_2(dbptH)Cl]$ (White)	69.11 (69.05)	6.12 (6.14)	3.01 (3.16)	7.17 (7.16)	3.58 (3.61)	3.38 (4.00)	142	91
(5) $[Cu(PPh_3)_2(dbptH)Br]$ (White)	65.73 (65.76)	5.78 (5.84)	3.03 (3.01)	6.80 (6.82)	3.43 (3.44)	8.61 (8.58)	150	86
(6) $[Cu(PPh_3)_2(dbptH)I]$ (White)	62.56 (62.60)	5.53 (5.56)	2.87 (2.86)	6.48 (6.49)	3.31 (3.28)	12.99 (12.97)	141	93
(7) $[Cu(PPh_3)_2(tzdtH)Cl]$ (Yellowish white)	63.11 (63.06)	4.73 (4.75)	2.00 (1.89)	8.45 (8.55)	8.56 (8.60)	4.90 (4.90)	204	87
(8) $[Cu(PPh_3)_2(tzdtH)Br]$ (Yellowish white)	59.48 (59.50)	4.45 (4.48)	1.80 (1.78)	8.10 (8.07)	8.05 (8.10)	10.21 (10.15)	179d	77
(9) $[Cu(PPh_3)_2(tzdtH)I]$ (Yellowish white)	65.12 (65.15)	4.20 (4.23)	1.69 (1.68)	7.65 (7.62)	7.71 (7.70)	15.14 (15.20)	171d	72

d = decomposed.

complexes are given in Figures 4.1 and 4.2 respectively and the data are summarized in Table 4.2. Both the ligands adopt the thione form in the free state and in their complexes. This is evident by the absence of the ν(SH) band in the region of 2500 cm^{-1} and by the presence of ν(NH) in the range 2890 to 3310 cm^{-1}. Both the ligands contain thioamide group (H-N-C=S) and should give rise to four characteristic thioamide bands namely I, II, III and IV in the region of 1500, 1300, 1000 and 800 cm^{-1} and have contribution from ν(C-N)+δ(N-H); ν(C=S)+ν(C=N)+ν(C-H); ν(C-N)+ν(C-S) and ν(C-S) modes of vibrations respectively. All these bands are found for the ligand dmptH but the III band of ligand dbptH is too weak to be observed, Figure 4.2. The other bands useful for identification of donor atoms are ν(NH) and ν(C=S). All complexes exhibited the characteristic bands of triphenylphosphine.[76] The mode of ligand bonding has been decided on the basis of shifts on complexation of ν(NH), ν(C=S) and four thioamide bands, Figure 4.1 and 4.2. The II and III thioamide bands have contributions from ν(CN) and ν(CS) vibrations but ν(CS) contributes more than ν(CN) to the thioamide band II,[231] therefore, band II can be utilized to decide the coordination site but it is difficult to decide the coordination site on the basis of shifts of band III.

The band at 3310 cm^{-1} and 3230 cm^{-1} assigned to ν(NH)

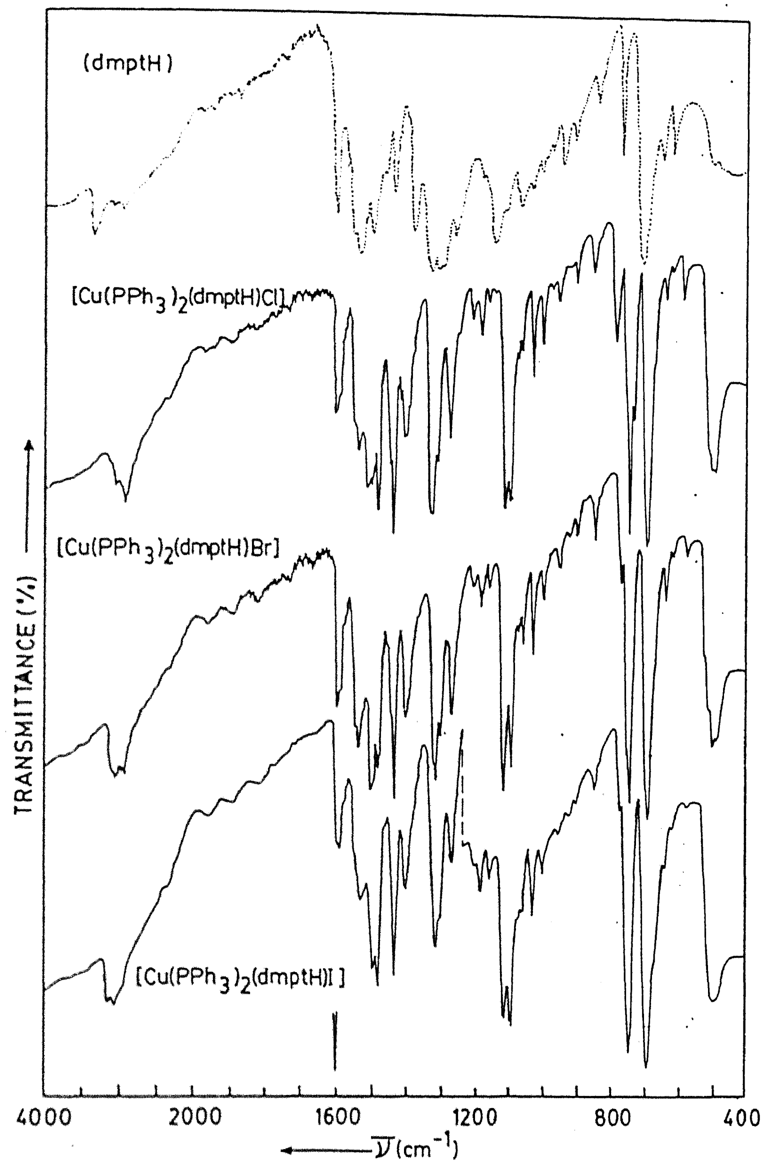


Figure 4.1. The IR spectra of the ligand dmptH and its complexes.

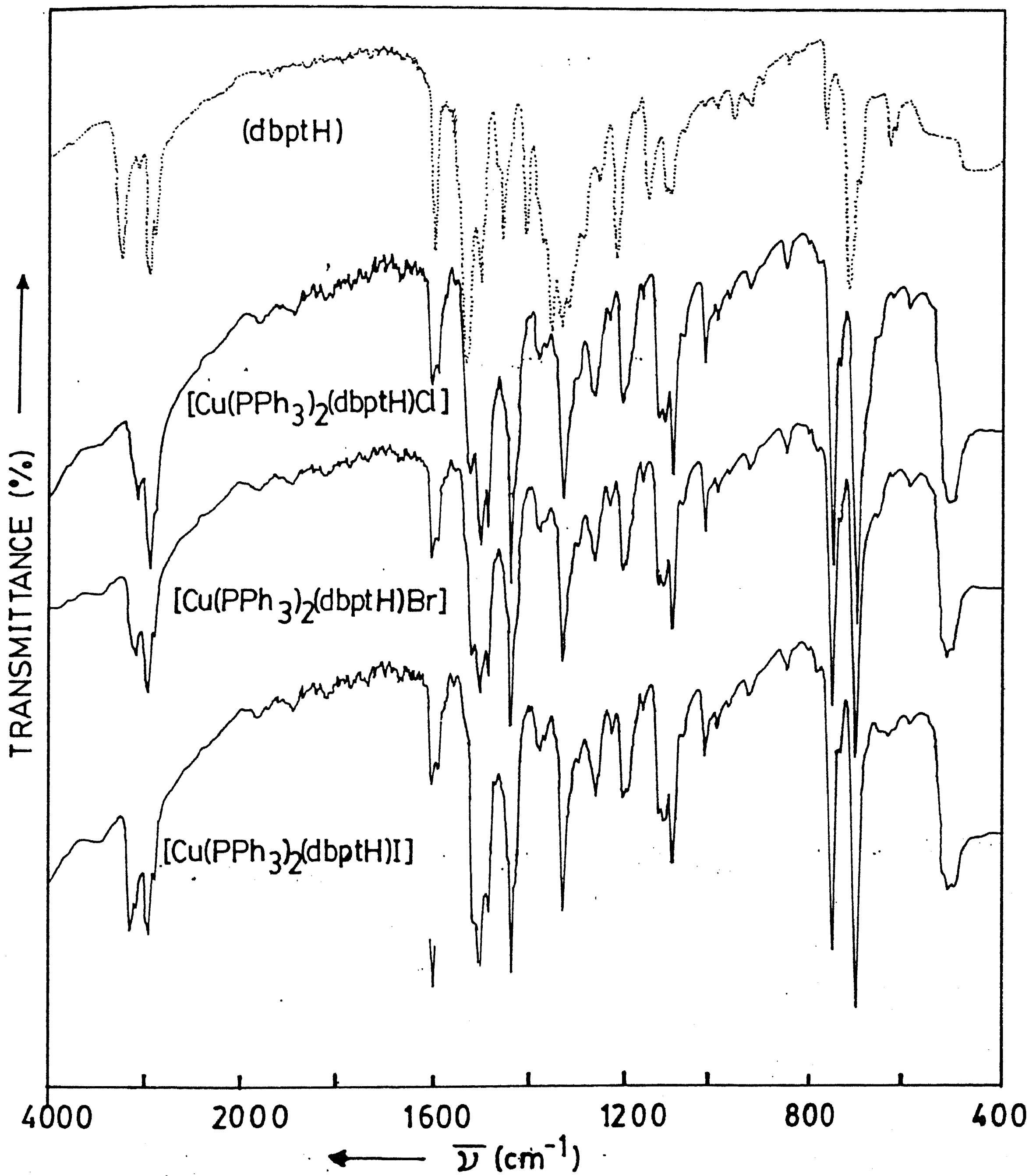


Figure 4.2. The IR spectra of the ligand dbptH and its complexes.

Table 4.2. Major IR bands of dmptH, dbptH and their complexes (cm^{-1})

	Compound	ν(NH)	ν(C=S)	Thioamide bands I	II	III	IV
	Ligand (dmptH)	3310	1045	1595	1325	1065	770
		2950		1535	1300		710
(1)	$[Cu(PPh_3)_2(dmptH)Cl]$	2950	1115	1605	1330	1070	785
				1540	1315		735
					1280		
(2)	$[Cu(PPh_3)_2(dmptH)Br]$	3100	1115	1600	1315	1060	770
		2950		1540	1305		750
		2900			1270		
(3)	$[Cu(PPh_3)_2(dmptH)I]$	3150	1120	1595	1315	1065	775
				1540	1305sh		
					1270		
	Ligand (dbptH)	3230	1150	1595	1355	——	765
		2940		1530	1330		715
		2890		1505	1320		
(4)	$[Cu(PPh_3)_2(dbptH)Cl]$	2940	1125	1605	1325	——	730
		2890sh		1520			
				1505			
(5)	$[Cu(PPh_3)_2(dbptH)Br]$	2950	1125	1600	1325	——	730
		2895		1520			
				1500			
(6)	$[Cu(PPh_3)_2(dbptH)I]$	3150	1125	1605	1325	——	730
		2950		1515sh			
				1500			

sh = shoulder.

for both the ligands dmptH and dbptH respectively, Figures 4.1 and 4.2, becomes too weak to be observable in the IR spectra of the complexes. The thioamide band I, having contribution from ν(C-N)+δ(N-H) shifts slightly towards the higher region indicating non-involvement of the NH group on coordination. The thioamide bands II, having more contribution from ν(CS) undergo red shift or splits in which intense bands are observed in the lower frequency region, Figures 4.1 and 4.2. In the case of compound (1) the broad thioamide band II of ligand dmptH at 1325 cm^{-1} and 1300 cm^{-1} splits into three bands *ca* 1330 cm^{-1} 1315 cm^{-1} and 1280 cm^{-1}, Figure 4.1, and in the compound (2) and (3) these bands are observed at 1315, 1305 and 1270 cm^{-1}, Figure 4.1. The broad thioamide band II of the ligand dbptH is observed at 1355, 1330 and 1320 cm^{-1} and becomes sharp single band at 1325 cm^{-1} on complexation, Figure 4.2. These shifts indicate the involvement of C=S group in coordination. This is also supported by the red shift of the ν(C=S) band *ca* $\Delta\bar{\nu}$ = 25-30 cm^{-1} and the red shift or splitting of the thioamide band II, Figures 4.1 and 4.2. The bands observed at 770 cm^{-1} and 710 cm^{-1} for the ligand dmptH, Figure 4.1, and at 765 cm^{-1} and 715 cm^{-1} for the ligand dbptH, Figure 4.2 are assigned as thioamide band IV. The band at 770 cm^{-1} splits into two *ca* $\Delta\bar{\nu}$ = 50 and 20 cm^{-1} for the compounds (1), (2) and for compound

(3) the band is not discernible, Figure 4.1. The band at 710 cm^{-1} in the compounds is absent which may be coupled with the band due to phenyl groups[14] at 695 cm^{-1}, Figure 4.1. The band at 765 cm^{-1}, Figure 4.2, splits into two bands *ca* 780 and 730 cm^{-1} or shifts to 730 cm^{-1}, Figure 4.2, in all the three compounds (4), (5) and (6) and the band at 715 cm^{-1} is not observed in the complexes. All these observations clearly indicate the involvement of C=S group in the coordination. Bonding through sulphur atom is also favoured because copper(I), being soft, should prefer to interact with a soft donor such as sulphur and indeed the presence of sulphur-copper(I) bond is confirmed by X-ray single structure of many complexes of ligands having thioamide group[245] and of substituted thiourea ligands.[250] Specially Cu^{I}—S bond with heterocyclic thione donors having thioamide groups[29,106,66,68] have been extensively studied.

Four thioamide bands of the ligand tzdtH, I at 1490 cm^{-1}, II at 1245 cm^{-1}, III at 990 cm^{-1} and IV at 690 cm^{-1}, 650 cm^{-1} are assigned by Preti and Tosi[117] who reported various complexes including copper(I) with the deprotonated ligand. Vibrational analysis of the ligand has been carried out by Devillanova et al,[231] who also reported the various copper(I) complexes[112] with the neutral ligand. The bands at 690 and 650 cm^{-1} which are assigned to ν(CS) *sym* and *asym* by

Preti and Tosi[117] are assigned mainly due to Δ(NH) and $\nu(C_1S_1)$ (C_1 = carbon atom bonded with ring sulphur, S_1 = ring sulphur) respectively by Devillanova et al.[231] Keeping this difference of opinion in mind we have taken various other bands to decide the coordination site. The IR spectra of the free ligand, tzdtH, and its complexes are given in Figure 4.3 and the principal bands are collected in the Table 4.3. This ligand, tzdtH, is also bonded to the metal through the thione sulphur as shown by the shifts of the ν(CS) and ν(CN)+δ(NH) bands, Figure 4.3. The IR bands namely, ν(NH) at 3130 cm^{-1}, ν(CN)+δ(NH) at 1500 cm^{-1}, ν(CS) at 1085 cm^{-1} and 545 cm^{-1}, $\nu(CS_1)+\delta$(CS)+ring def; (C = carbon atom bonded with thione sulphur and ring sulphur) at 585 cm^{-1}, $\nu(C_1S_1)$ + ring def at 653 cm^{-1} and Δ(CS) at 435 cm^{-1} of the free ligand,[231] Figure 4.3, have been used to decide the donor site. Comparison of the IR spectra of the free ligand with its complexes shows that ν(CS) band at 1085 cm^{-1} either couples with the characteristic band of triphenylphosphine[76] at 1088 cm^{-1} or absent and the band at 545 cm^{-1} Figure 4.3, probably shifts to the lower frequency region and couples with the band around 505 cm^{-1} of the complex $[Cu(PPh_3)_3X]$.[59] The Δ(CS) band at 435 cm^{-1} of the ligand is absent in the IR spectra of the complexes, Figure 4.3. This shows the major shift of the band ν(CS) at 545 cm^{-1} and the band Δ(CS) at 435 cm^{-1} to the

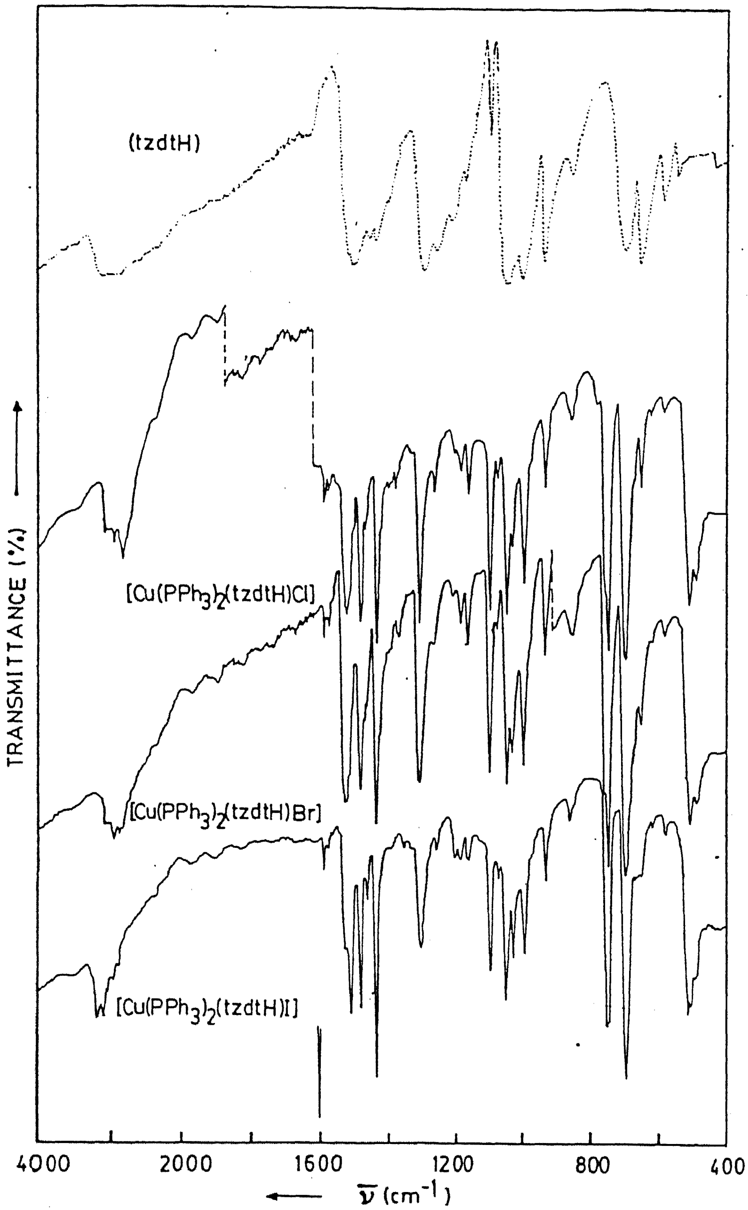


Figure 4.3. The IR spectra of the ligand tzdtH and its complexes.

Table 4.3. Major IR bands of tzdtH and its complexes (cm^{-1})

Compound	$\nu(NH)$	$\nu(CN)+\delta(NH)$	$\nu(CS_1)$	$\nu(CS)$	$\Delta(CS)$	Vibrations between 600 and 400 cm^{-1}
Ligand (tzdtH)	3130-2700	1500	653 585	1085 545	434	585, 545, 434
(7) [$Cu(PPh_3)_2$(tzdtH)Cl]	3050-2800	1520	655 585	——	——	585, 505, 485
(8) [$Cu(PPh_3)_2$(tzdtH)Br]	3050-2800	1525	655 585	——	——	585, 505, 485
(9) [$Cu(PPh_3)_2$(tzdtH)I]	3140-2900	1515	655 585	——	——	585, 520-490

lower region which indicates the involvement of thione sulphur in the coordination. Other bands at 585, 653 and 1500 cm^{-1} of the free ligand, Figure 4.3, are observed either as such or shift towards the higher frequency region due to complex formation, which indicates the non-involvement of the ring sulphur and NH group. The ν(NH) band which shifts to the lower region may be due to hydrogen bonding. In fact very recently many copper(I) complexes of the triphenylphosphine and the heterocyclic thione donors have been reported[66,70] of the same stoichiometry but with different heterocyclic thione donors and some of them have been characterized by single X-ray crystallography.

4.3.2 Electronic (UV-vis) and ^{1}H NMR Spectra

The electronic (UV-vis) spectra and the representative ^{1}H NMR spectra of the complexes and free ligands are given in Figures 4.4, 4.5, 4.6 and Figures 4.7, 4.8, 4.9 respectively and the data are collected in Table 4.4 with assignments. As expected only UV absorption bands are observed which are assigned as intra ligand (IL) bands, Figure 4.4, 4.5, 4.6. The ^{1}H NMR spectra of the complexes clearly show the peaks due to the ligands and triphenylphosphines, Figures 4.7, 4.8, 4.9. On complexation the peaks shift slightly towards the higher magnetic field (lower δ value), Figures 4.7, 4.8, 4.9. These shifts towards lower δ values indicate the

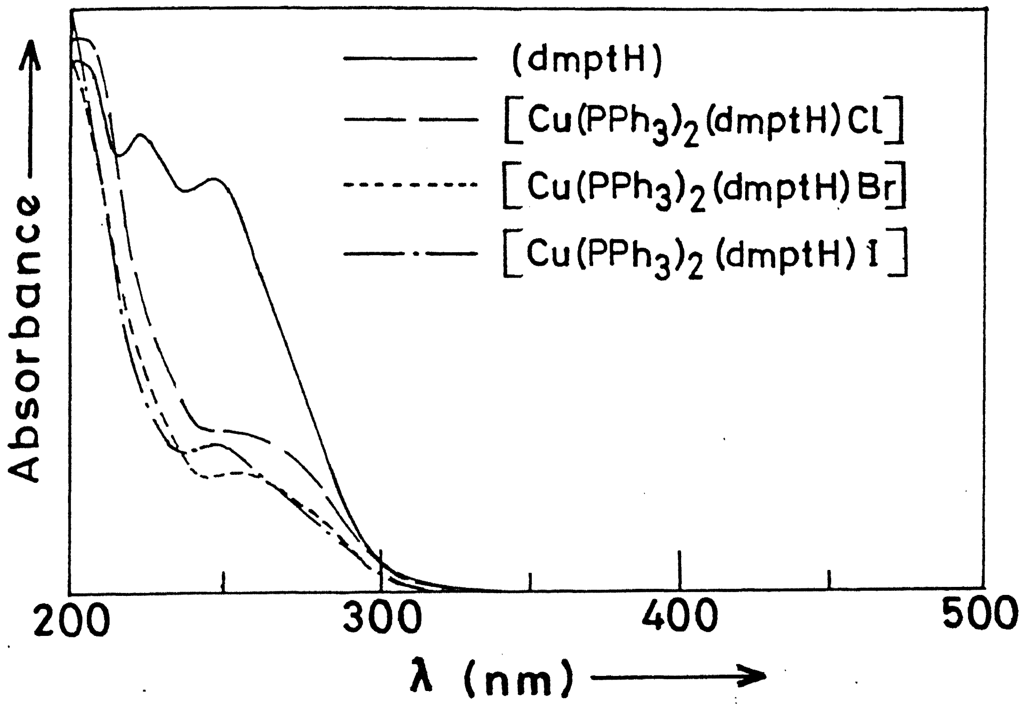


Figure 4.4. The electronic (UV-vis) spectra of the ligand dmptH and its complexes.

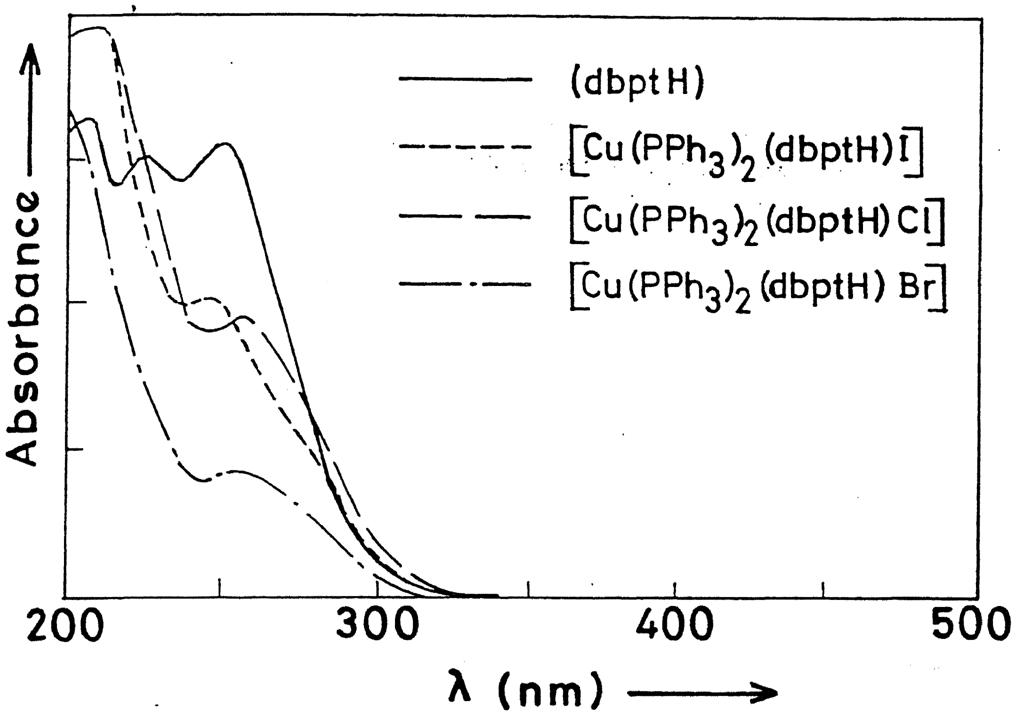


Figure 4.5. The electronic (UV-vis) spectra of the ligand dbptH and its complexes.

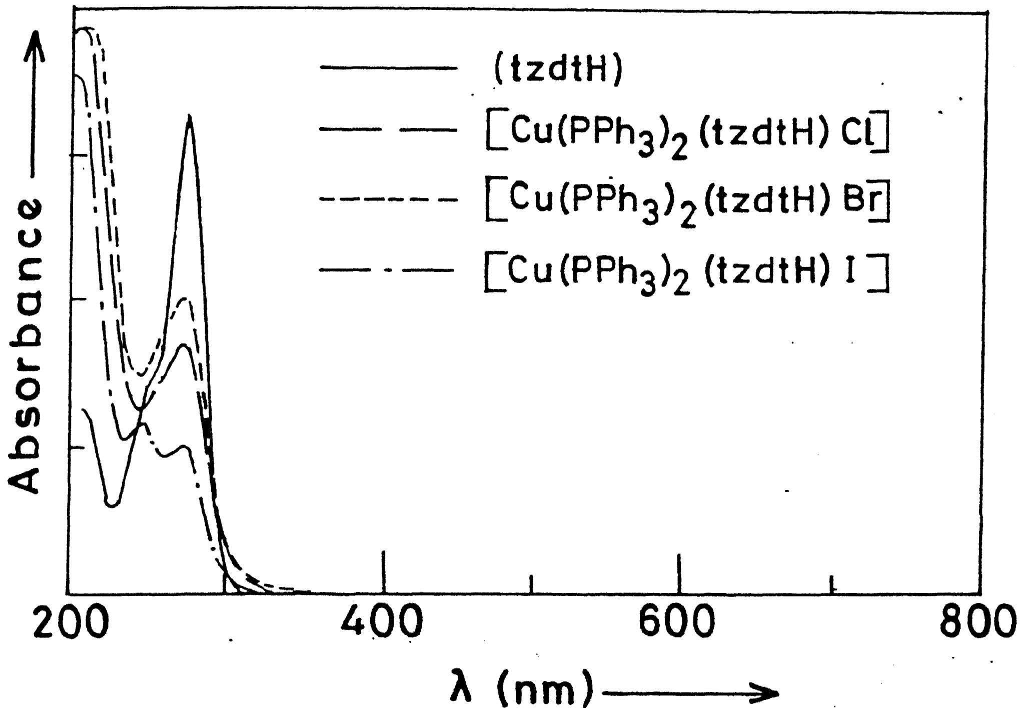


Figure 4.6. The electronic (UV-vis) spectra of the ligand tzdtH and its complexes.

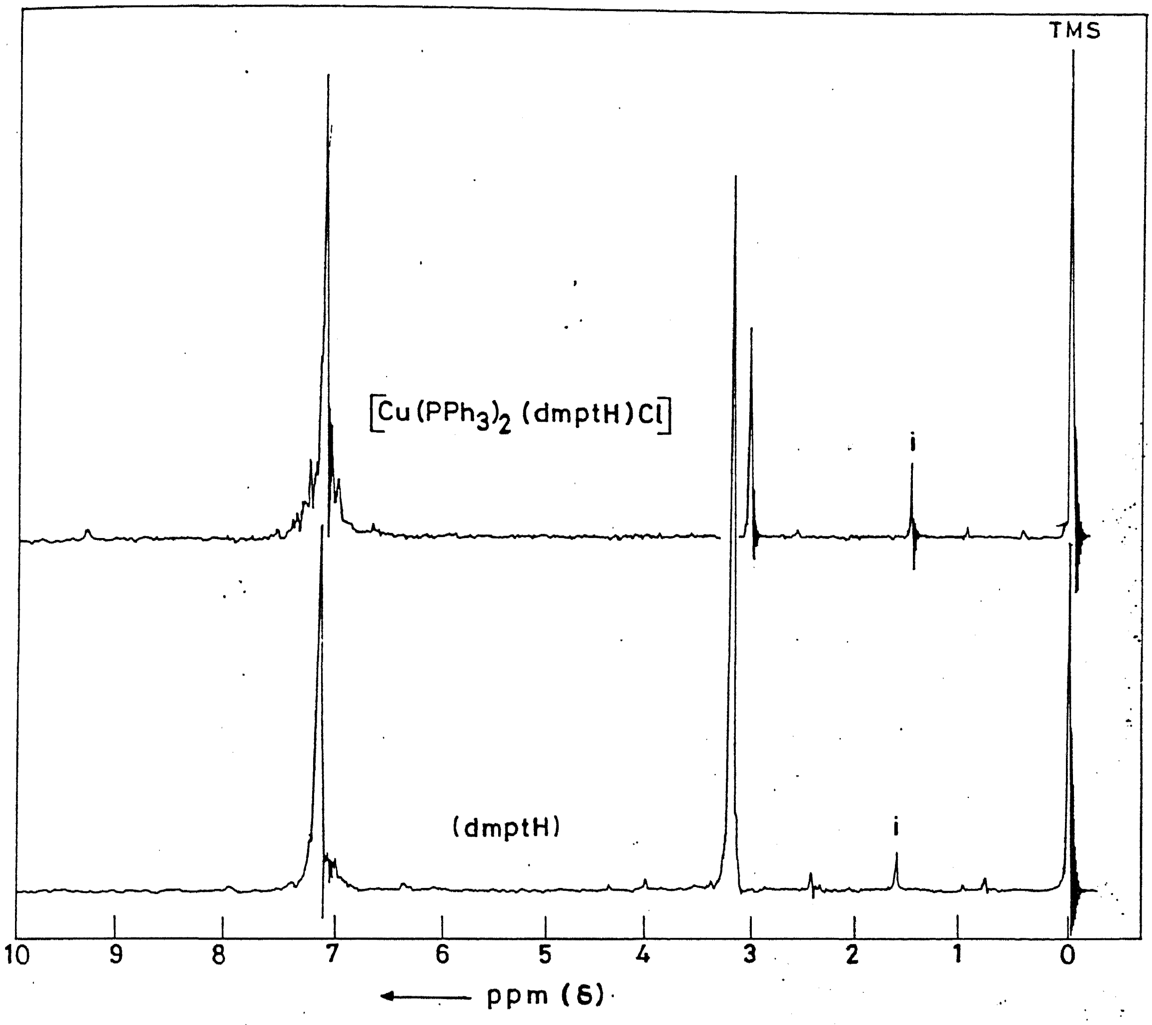


Figure 4.7. The ^{1}H NMR spectra of the ligand dmptH and its representative complex. The peaks indicated by i are due to the impurity.

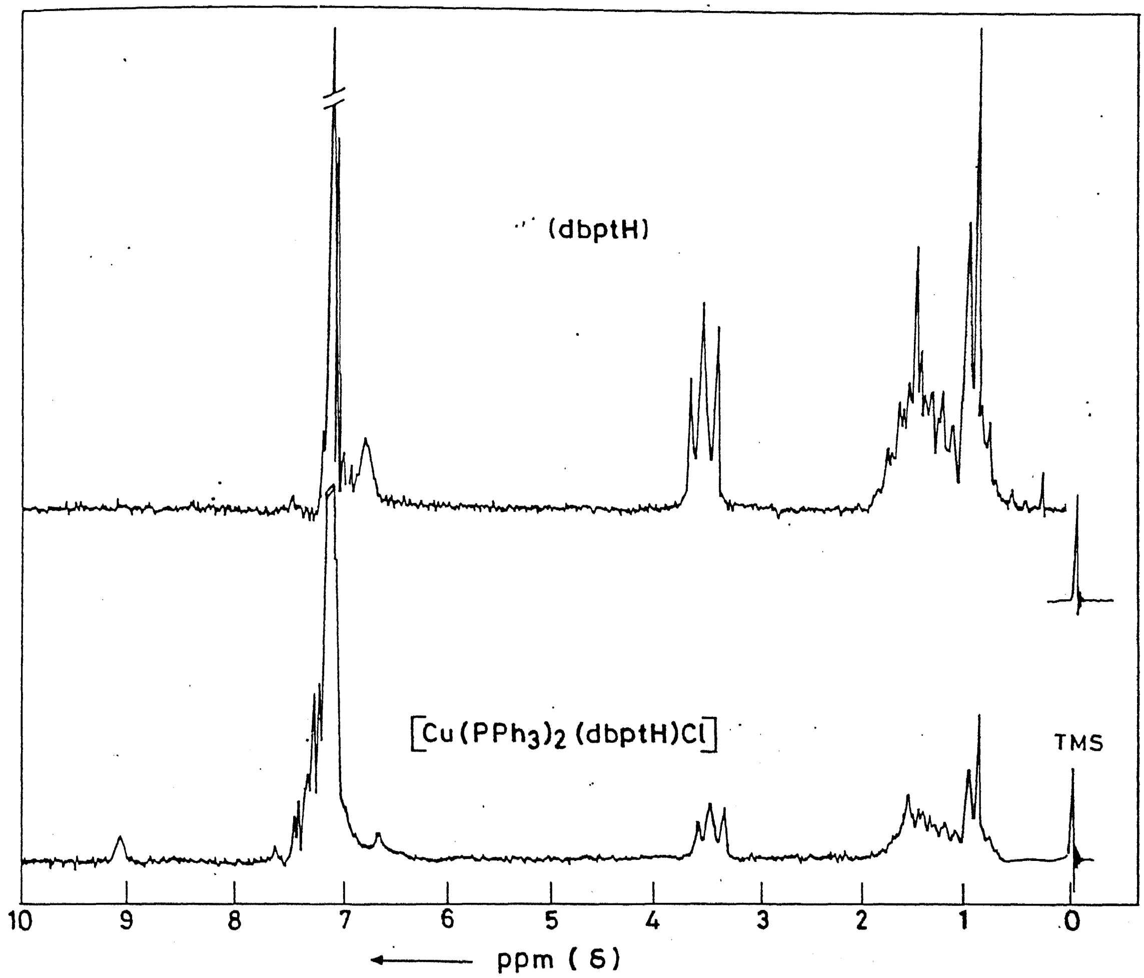


Figure 4.8. The ^{1}H NMR spectra of the ligand dbptH and its representative complex.

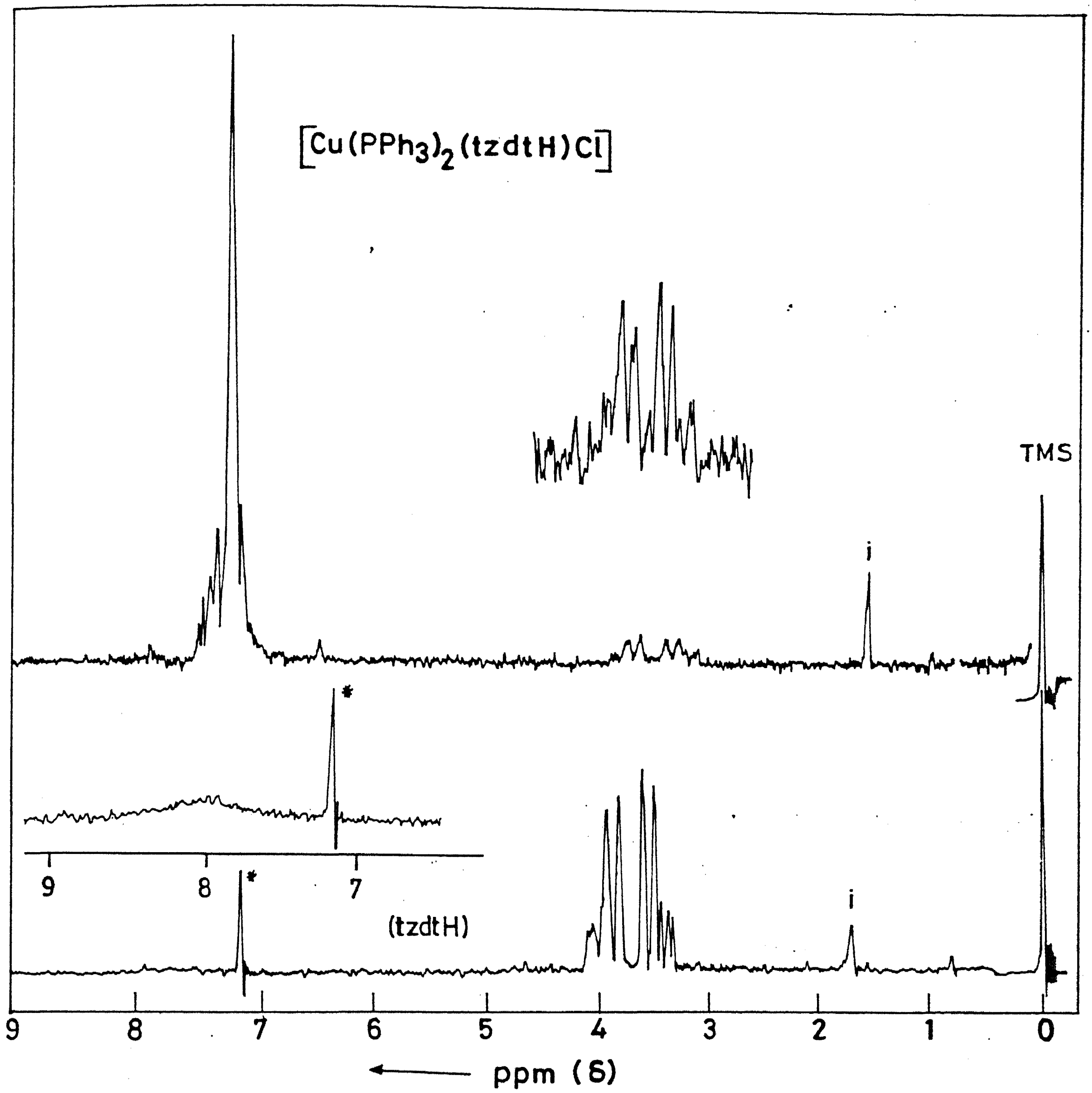


Figure 4.9. The ^{1}H NMR spectra of the ligand tzdtH and its representative complex. The peaks indicated by i are due to the solvent impurity and indicated by the asterisk are due to the $CHCl_3$ impurity.

Table 4.4. Electronic spectral data of the ligands and the complexes in CH_3CN and ^1H NMR spectral data of the ligands and complexes in $CDCl_3$

Compound	Band Position, λ_{max}(nm), with Assignments		^1H NMR Signal with Assignments ppm(δ)
1	2		3
Ligand (dmptH)	223.0		3.27 (s, 6H, $-N(CH_3)_2$ group);
	246.5		7.20 (s, 5H, $-C_6H_5$ group).
(1) $[Cu(PPh_3)_2(dmptH)Cl]$	253.0	IL	3.10 (s, 6H, $-N(CH_3)_2$ group);
			7.00–7.50 (m, 35H, $-C_6H_5$ groups);
			9.37 (s[broad], 1H, >NH group).
(2) $[Cu(PPh_3)_2(dmptH)Br]$	250.0	IL	3.13 (s, 6H, $-N(CH_3)_2$ group);
			7.00–7.50 (m, 35H, $-C_6H_5$ groups);
			8.73 (s[broad], 1H, >NH group).
(3) $[Cu(PPh_3)_2(dmptH)I]$			3.10 (s, 6H, $-N(CH_3)_2$ group);
			7.00–7.50 (m, 35H, $-C_6H_5$ groups);
			8.43 (s[broad], 1H, >NH group).
Ligand (dbptH)	207.0		0.67–2.00 (m, 6H, $-CH_3$ groups);
	225.0		3.63 (t, 12H, $-CH_2$ groups);
	251.0		6.67–7.33 (m, 35H, $-C_6H_5$ groups)
(4) $[Cu(PPh_3)_2(dbptH)Cl]$	212.0	IL	0.67–1.80 (m, 6H, $-CH_3$ groups);
	255.0	IL	3.50 (t, 12H, $>CH_2$ groups);
			6.83–7.50 (m, 35H, $-C_6H_5$ groups);
			9.03 (s[broad], 1H, >NH group).

Table 4.4 (contd...)

1	2		3
(5) $[Cu(PPh_3)_2(dbptH)Br]$	256.5	IL	0.67–1.83 (m, 6H, $-CH_3$ groups);
			3.50 (t, 12H, $>CH_2$ groups);
			7.00–7.67 (m, 35H, $-C_6H_5$ groups);
			8.57 (s[broad], 1H, >NH group).
(6) $[Cu(PPh_3)_2(dbptH)I]$	211.5	IL	0.67–1.83 (m, 6H, $-CH_3$ groups);
	247.0	IL	3.53 (t, 12H, $>CH_2$ groups);
			6.83–7.40 (m, 35H, $-C_6H_5$ groups);
			7.93 (s[broad], 1H, >NH group).
Ligand (tzdtH)	276.0		3.27–4.17 (m, 4H, $>CH_2$ groups);
			9.97 (s[broad], 1H, >NH group).
(7) $[Cu(PPh_3)_2(tzdtH)Cl]$	208.0	IL	3.07–3.73 (m, 4H, $>CH_2$ groups);
	274.0	IL	6.83–7.67 (m, 30H, $-C_6H_5$ groups).
(8) $[Cu(PPh_3)_2(tzdtH)Br]$	215.0	IL	3.07–3.70 (m, 4H, $>CH_2$ groups);
	274.0	IL	6.83–7.67 (m, 30H, $-C_6H_5$ groups).
(9) $[Cu(PPh_3)_2(tzdtH)I]$	248.0	IL	3.07–3.73 (m, 4H, $>CH_2$ groups);
	275.0	IL	6.83–7.67 (m, 30H, $-C_6H_5$ groups).

non-involvement of nitrogen atom (dmptH and dbptH) and nitrogen and ring sulphur atoms (tzdtH) as donor sites in the respective complexes. The ^{1}H NMR signals due to the >NH group of the ligands dmptH and dbptH are not discernible, whereas for the ligand tzdtH it is observed as a very broad weak signal. The ^{1}H NMR signal of the >NH proton in the complexes of dmptH and dbptH are observed as a broad signal whereas the >NH proton signal of the ligand tzdtH in its complexes are not observed. The broadening of the signals may be due to hydrogen bonding.[29,73,68] The δ value decreases as the halogen atomic radius increases,[68] Figures 4.10 and 4.11. This observation indicates the gradual weakening of hydrogen bond from chloride to bromide to iodide complexes. The >NH proton signal (δ value) is independent on concentration, indicating the intramolecular hydrogen bonding in the complexes. The proportions of the protons, observed by integration are in good agreement with the proposed stoichiometry of the complexes.

4.3.3 ^{13}C and ^{31}P NMR Chemical Shifts

The ^{13}C and ^{31}P NMR spectral data of the representative complexes are given in Figures 4.12 and 4.13 respectively and the data are collected in Table 4.5, with assignments. Data of triphenylphosphine, tetramethylthiourea and N,N′-diethylaniline are also given in the Table 4.5 from

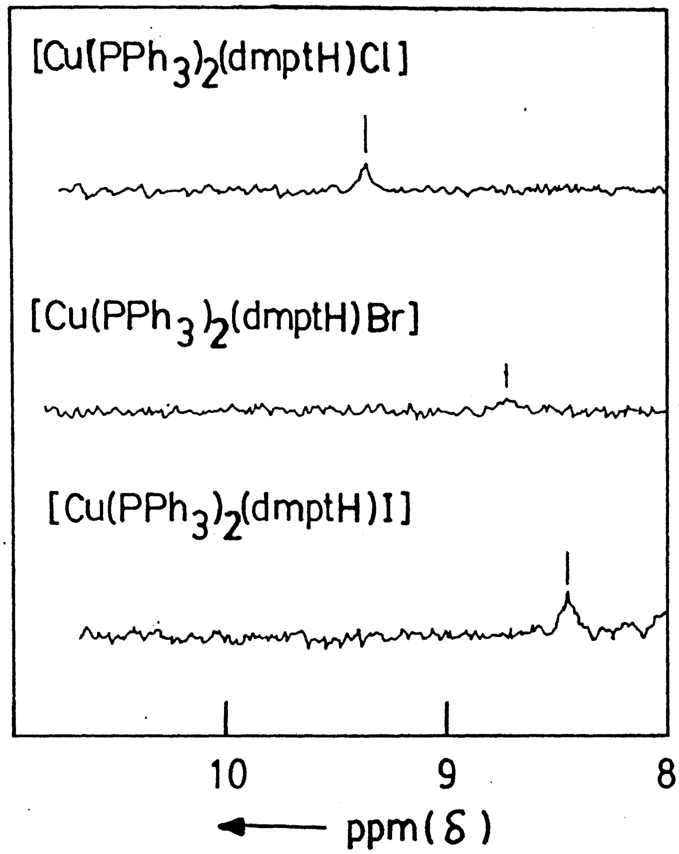


Figure 4.10. The ^1H NMR signals of the dmptH complexes in the >NH region.

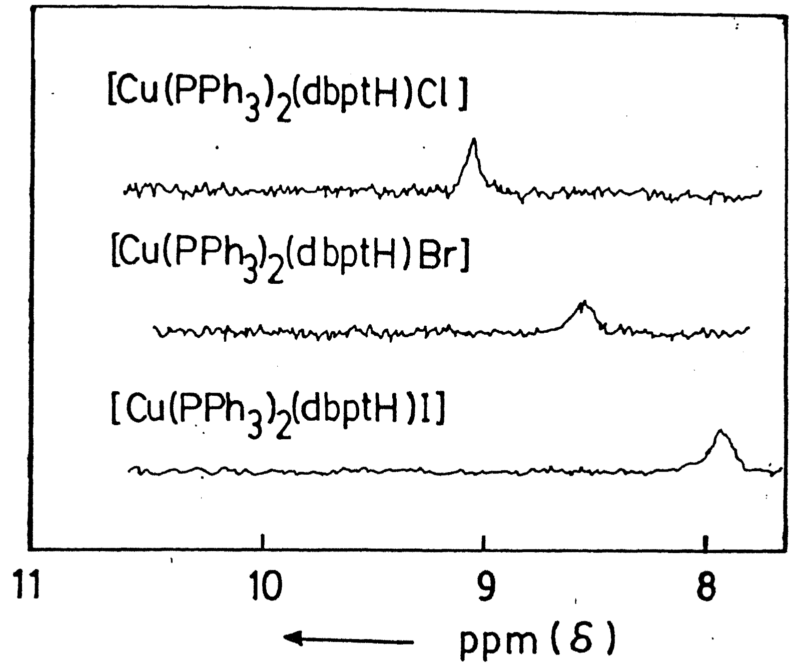


Figure 4.11. The ^{1}H NMR signals of the dbptH complexes in the >NH region.

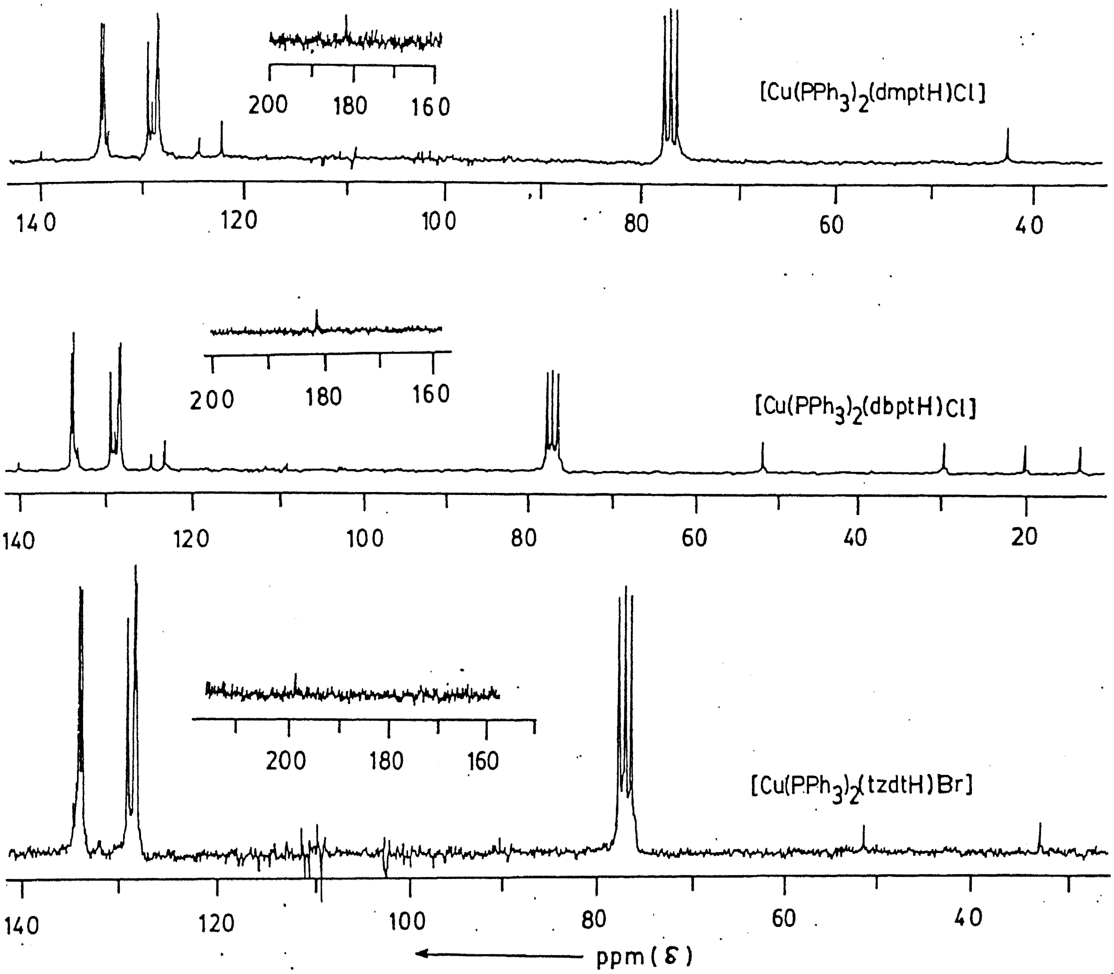


Figure 4.12. The ^{13}C NMR spectra of the representative complexes of ligands dmptH, dbptH and tzdtH.

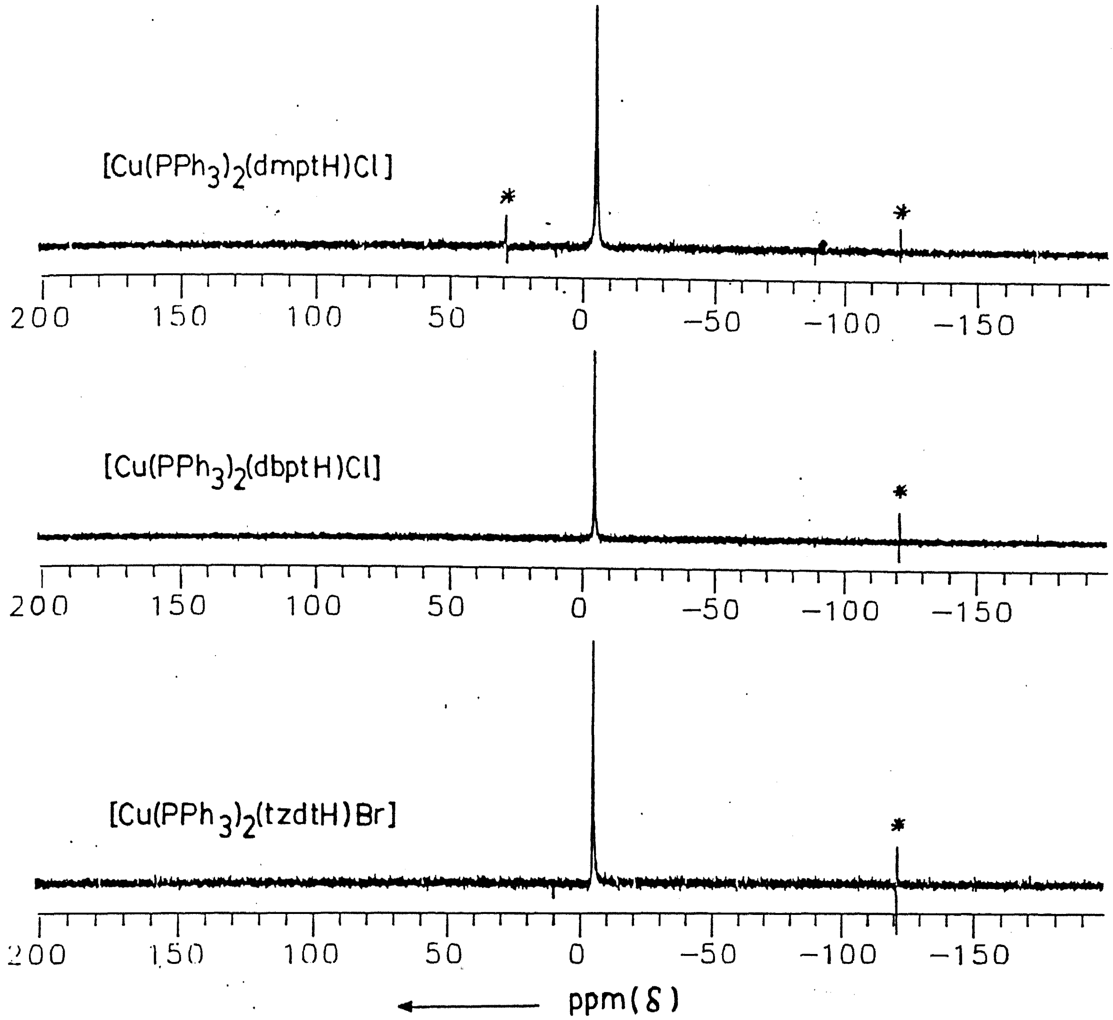
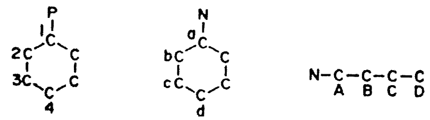


Figure 4.13. The ^{31}P NMR spectra of the representative complexes of ligands dmptH, dbptH and tztdH. The peaks indicated by asterisk are due to the electrical spikes.

Table 4.5. ^{13}C NMR chemical shifts (δ/ppm from Me_4Si) and ^{31}P NMR chemical shifts (δ/ppm from 85% H_3PO_4 ext. ref.) of representative complexes in $CDCl_3$, peak multiplicities in brackets



Compounds	^{13}C NMR 1	2	3	4	a	b	c	d	Other peaks	^{31}P NMR
(1) $[Cu(PPh_3)_2(dmptH)Cl]$	—	133.91(2)	128.41(2)	129.42(1)	139.50(1)	122.23(1)	128.91(1)	124.48(1)	181.04(1) C=S; 42.50(1) N—CH_3	−4.89(1)
(4) $[Cu(PPh_3)_2(dbptH)Cl]$	—	133.93(2)	128.43(2)	129.45(1)	140.08(1)	122.92(1)	129.08(1)	124.68(1)	180.84(1) C=S; 51.55(1)A; 29.13(1)B; 19.77(1)C; 13.72(1)D	−4.94(1)
(8) $[Cu(PPh_3)_2(tzdtH)Br]$	—	133.96(2)	128.33(2)	129.16(1)	—	—	—	—	198.92(1) C=S; 51.30(1) N—C; 32.65(1) S—C	−5.50(1)
PPh_3[a]	137.2(2)	133.6(2)	128.4(2)	128.5(1)	—	—	—	—	—	−6.00(1)
$SC[N(CH_3)_2]_2$[b]	—	—	—	—	—	—	—	—	193.9(1) C=S; 43.0(1) N—C	—
Ph—$N(C_2H_5)_2$[b]	—	—	—	—	147.8(1)	112.0(1)	129.1(1)	115.5(1)	44.2(1) N—CH_2—; 12.5(1) —CH_3	—

[a] ^{13}C NMR data from ref. 77. ^{31}P NMR data from ref. 256.
[b] ^{13}C NMR data from ref. 77.

literature for comparison and assignment. In the substituted thiourea and in metal complexes the ^{13}C NMR signals for C=S carbon[77,251,252] are found in the range of 180-194 ppm(δ), which are in very good agreement with our observations. The ^{13}C NMR data of 1,3-thiazolidine-2-thione are given as 51.3, 33.8 and 202.0 ppm(δ) for C-N, C-S and C=S carbon atoms respectively.[238] In the tzdtH complexes there is very slight shift towards higher field (lower δ value). Other peaks due to phenyl rings and alkyl groups are observed in the expected characteristic region, Figure 4.12. As expected only one sharp ^{31}P NMR signal of triphenylphosphine is observed, Figure 4.13, in all the complexes with a shift towards lower field (higher δ value) in comparison to free triphenylphosphine.[78,253] The shifting of the ^{31}P NMR signal to the lower field in comparison to the free triphenylphosphine is expected as on coordination the electron density shifts from phosphorus atom to the copper which results in the deshielding of the phosphorus nuclei. This is also in accordance with the higher σ-donating than the π-accepting property of the triphenylphosphine ligand.

4.4 SUMMARY

Reactions of $[Cu(PPh_3)_3X]$ with title ligands yield $[Cu(PPh_3)_2(LH)X]$. The complexes have been characterized on

the basis of analytical data, IR, electronic (UV-vis), ^{1}H, ^{31}P and ^{13}C NMR spectral studies, conductivity and magnetic measurements. In all cases there is a distorted tetrahedral environment around copper(I) and the ligands (LH) bind through thione sulphur atom to copper(I).

CHAPTER 5*

SYNTHESIS AND CHARACTERIZATION OF $[Cu(AsPh_3)_2(LH)X]$ (LH = dmptH, dbptH, tzdtH; X = Cl, Br, I)

5.1 INTRODUCTION

The triphenylarsine analogues of the complexes reported in the previous chapter have been synthesized and characterized in this chapter.

5.2 EXPERIMENTAL

5.2.1 Starting Materials

All the chemicals used are either of Analar or chemically pure grade. The ligands N,N-dimethyl-N'-phenylthiourea (dmptH) and N,N-dibutyl-N'-phenylthiourea (dbptH) have been prepared by the direct addition of phenyl isothiocyanate to the appropriate secondary amine in methanol in 1:1 ratio as described in the previous chapter. The ligand

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* R. Singh and S. K. Dikshit, (manuscript under preparation).

1,3-thiazolidine-2-thione has been recrystallized from hot water before use. The copper(I) halides have been prepared as described in chapter 2.

5.2.2 Physical Methods

Sulphur, halides and copper have been estimated gravimetrically as described in chapter 2. The carbon, hydrogen and nitrogen analyses have been done at the Regional Sophisticated Instrumentation Center, Central Drugs Research Institute, Lucknow, India. The IR and ^1H NMR spectra and conductivity, magnetic and melting point measurements have been carried out exactly as described in previous chapter except dmso-d_6 has been used as solvent for the ^1H NMR spectra of tzdtH complexes due to their low solubility in $CDCl_3$.

5.2.3 Preparation of Compounds

5.2.3(a) Preparation of $[Cu(AsPh_3)_2(dmptH)X]$

A mixture of CuX (1 mmol) and $AsPh_3$ (4 mmol) is refluxed on water bath with constant stirring in benzene (50 mL) till the reaction mixture becomes a clear solution (~20 minutes for Cl, Br and >30 minutes for I). The solution obtained is cooled to the room temperature and 1 mmol of the ligand is added with constant stirring. The solution immediately becomes pale yellow, which is stirred for about 3 hours at

room temperature. The volume of the reaction mixture is reduced to about 5 mL and step wise addition of petroleum ether (60-80°C) with constant shaking, initiates the precipitation of the desired complexes as yellowish white turbidity. The addition of petroleum ether is stopped at a point where turbidity is just dissolved on shaking and the clear solution is left for slow evaporation at room temperature overnight, whereupon fine crystals of the complex appear and are separated by centrifugation and washed several times with petroleum ether and dried *in vacuo* over P_4O_{10} for several hours. The complexes can also be separated by continuous excess addition of the petroleum ether (~100 mL) with constant shaking, but the particle size of the compounds obtained in this way is small or almost in powder form.

5.2.3(b) Preparation of [Cu($AsPh_3$)$_2$(dbptH)X]

For the preparation of these complexes the above method of preparation for the dmptH complexes has been followed but in case of bromide complex, it is isolated during reaction and therefore the following method for preparation of tzdtH complexes has been used.

5.2.3(c) Preparation of [Cu($AsPh_3$)$_2$(tzdtH)X]

A mixture of CuX (1 mmol) and $AsPh_3$ (4 mmol) is refluxed on water bath with constant stirring in benzene (50 mL) till the reaction mixture becomes clear solution (~20 minutes for

Cl, Br and >30 minutes for I). The solution obtained is cooled to the room temperature and 1 mmol of the ligand is added with constant stirring. The solution immediately becomes pale yellow, which is stirred for about 3 hours at room temperature. During the course of reaction, the desired complex is precipitated. The volume of the reaction mixture is reduced to about 5 mL and an excess petroleum ether (~100 mL) is added with constant shaking to insure the complete precipitation of the complex and left for few hours to settle. The complexes thus obtained are separated by centrifugation and washed several times with petroleum ether (60-80°C) and dried *in vacuo* over P_4O_{10} for several hours.

M. p., colour and yield of the complexes are given in Table 5.1 along with the analytical data.

5.3 RESULTS AND DISCUSSION

Analytical data of the complexes are in Table 5.1 which are consistent with the stoichiometries proposed. Conductivity measurements of the complexes in acetonitrile or nitrobenzene solution indicate the non-electrolytic nature of the complexes.[240] All complexes are diamagnetic at room temperature.

Table 5.1. Analytical data, colour, melting point (M. p.) and yield of the complexes

Compound	Found (Calculated) % C	H	N	Cu	S	Halide	M. p. ($\theta/^{0}C$)	Yield (%)
(1) [$Cu(AsPh_3)_2$(dmptH)Cl] (pale yellow)	60.4 (60.6)	4.9 (4.8)	3.0 (3.1)	7.1 (7.1)	3.5 (3.6)	7.1 (7.0)	102	31
(2) [$Cu(AsPh_3)_2$(dmptH)Br] (cream white)	57.6 (57.7)	4.4 (4.5)	3.1 (3.0)	6.6 (6.8)	3.5 (3.4)	8.4 (8.5)	98	38
(3) [$Cu(AsPh_3)_2$(dmptH)I] (pale yellow)	55.2 (55.0)	4.4 (4.3)	2.8 (2.9)	6.6 (6.5)	3.3 (3.3)	12.8 (12.9)	154d	40
(4) [$Cu(AsPh_3)_2$(dbptH)Cl] (cream white)	62.7 (62.8)	5.7 (5.6)	2.8 (2.9)	6.5 (6.6)	3.2 (3.3)	3.6 (3.6)	112	94
(5) [$Cu(AsPh_3)_2$(dbptH)Br] (cream white)	60.2 (60.0)	5.2 (5.3)	2.9 (2.8)	6.2 (6.2)	3.0 (3.1)	7.9 (7.8)	127	96
(6) [$Cu(AsPh_3)_2$(dbptH)I] (pale yellow)	57.3 (57.4)	5.0 (5.1)	2.5 (2.6)	6.1 (6.0)	3.2 (3.0)	11.8 (11.9)	132d	35
(7) [$Cu(AsPh_3)_2$(tzdtH)Cl] (cream white)	56.5 (56.4)	4.2 (4.3)	1.8 (1.7)	7.6 (7.7)	7.8 (7.7)	4.3 (4.3)	178d	63
(8) [$Cu(AsPh_3)_2$(tzdtH)Br] (yellowish white)	53.4 (53.5)	4.1 (4.0)	1.7 (1.6)	7.2 (7.3)	7.4 (7.3)	9.0 (9.1)	185d	66
(9) [$Cu(AsPh_3)_2$(tzdtH)I] (pale yellow)	50.8 (50.8)	3.9 (3.8)	1.6 (1.5)	6.9 (6.9)	7.1 (7.0)	13.7 (13.8)	186d	60

d = decomposed.

5.3.1 IR Spectra

The title ligands contain H—N—C=S group which may adopt either the thione form H—N—C=S or the thiol form N=C—SH. IR spectra of the ligands dmptH, dbptH and their representative complexes are given in Figures 5.1 and 5.2 respectively and their major bands are summarized in Table 5.2. Both the ligands adopt the thione form in the free state and in their complexes. This is evident by the absence of the ν(SH) band in the region of 2500 cm^{-1} and by the presence of ν(NH) in the region 2890-3310 cm^{-1}, Figures 5.3 and 5.4. Both the ligands contain thioamide group (H—N—C=S) and should give rise to four characteristic thioamide bands namely I, II, III and IV in the region of 1500, 1300, 1000 and 800 cm^{-1} and have contributions from ν(C-N)+δ(N-H); ν(C=S)+ν(C=N)+ν(C-H); ν(C-N)+ν(C-S) and ν(C-S) modes of vibrations respectively. All these bands are found for the ligand dmptH but, band III of ligand dbptH is too weak to be observed. The other bands useful for identification of donor atoms are ν(NH) and ν(C=S). All complexes exhibit the characteristic bands of triphenylarsine.[76] The mode of ligand bonding is decided on the basis of shifts on complexation of ν(NH), ν(C=S) and four thioamide bands, Figures 5.1, 5.2, 5.3 and 5.4. The II and III thioamide bands have contributions from ν(CN) and ν(CS)

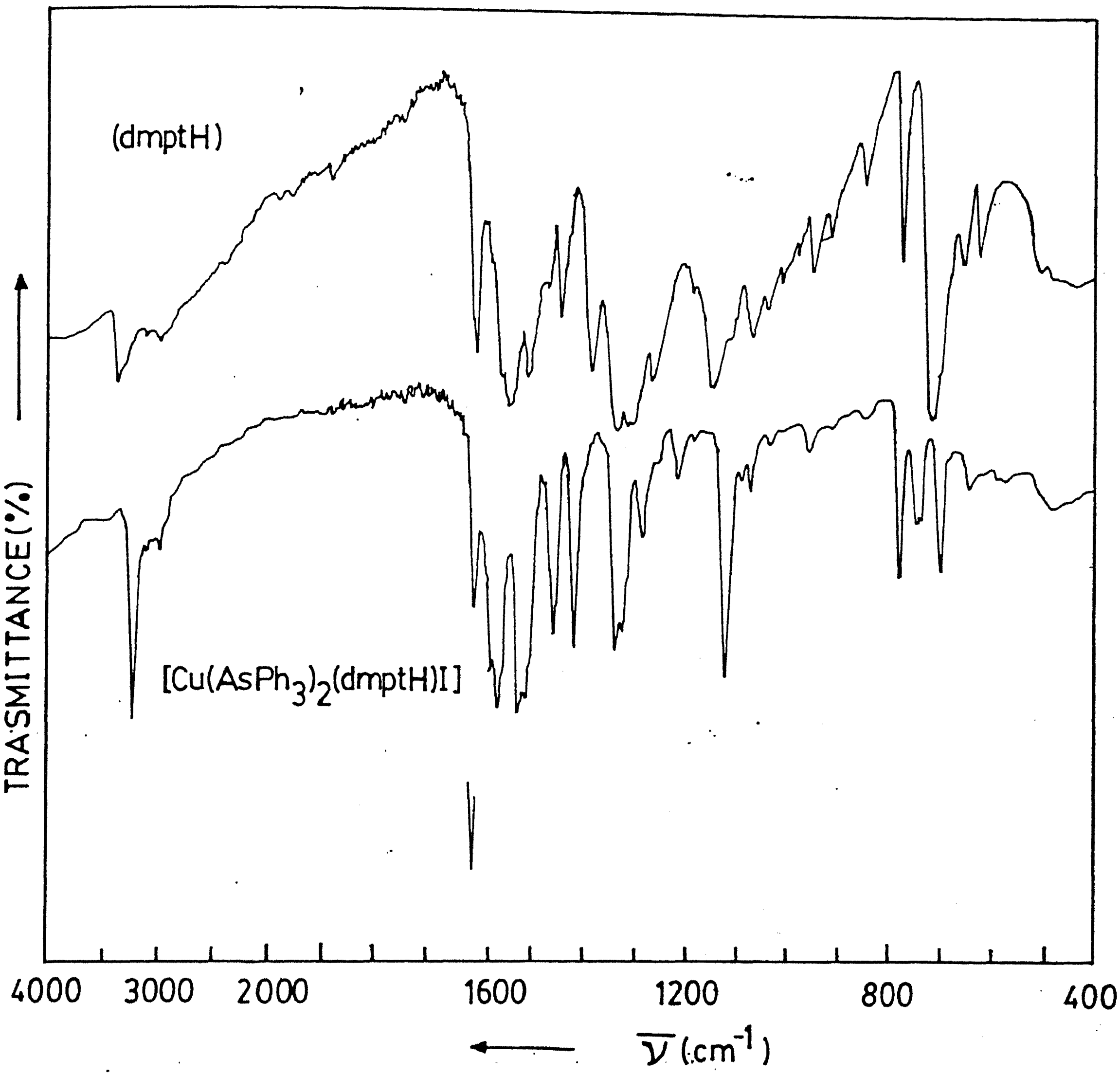

Figure 5.1. The IR spectra of the ligand dmptH and its representative complex.

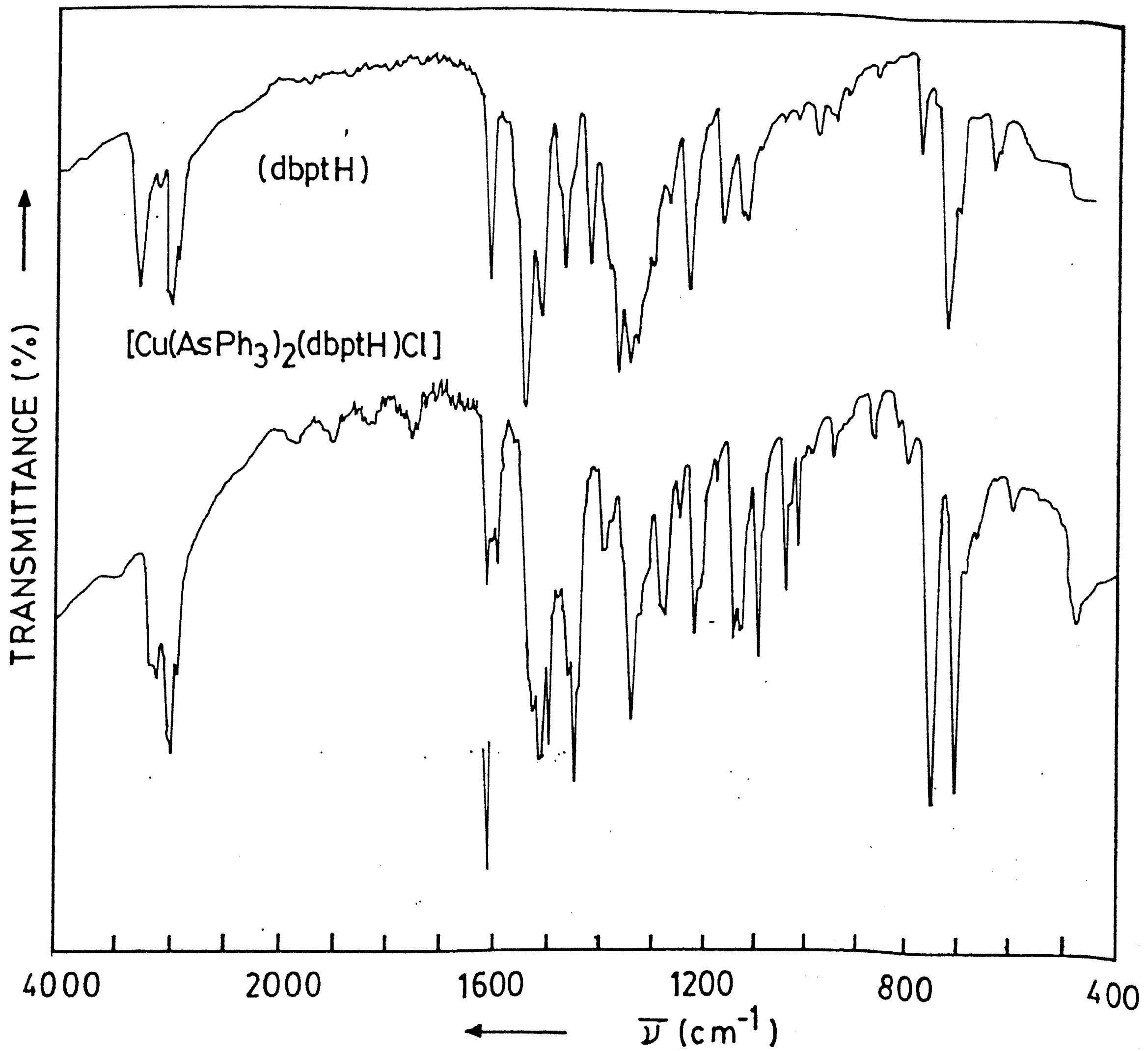

Figure 5.2. The IR spectra of the ligand dbptH and its representative complex.

Table 5.2. Major IR bands of dmptH, dbptH and their complexes (cm^{-1})

Compound	ν(NH)	ν(CS)	Thioamide bands I	II	III	IV
Ligand (dmptH)	3310-3340	1145	1595	1325	1065	770
			1535	1300		710
(1) $[Cu(AsPh_3)_2(dmptH)Cl]$	3150	1115	1600	1330	1070	770
			1535	1280		735
(2) $[Cu(AsPh_3)_2(dmptH)Br]$	3160	1115	1600	1315	1060	770
			1520	1275		750
(3) $[Cu(AsPh_3)_2(dmptH)I]$	3200	1115	1595	1325	1060	770
			1550	1315		735
				1270		
Ligand (dbptH)	3230	1150	1595	1355	——	765
			1530	1330		715
			1505	1320		
(4) $[Cu(AsPh_3)_2(dbptH)Cl]$	3150	1160	1600	1380	——	810
		1130	1525	1330		685
			1505	1245		
(5) $[Cu(AsPh_3)_2(dbptH)Br]$	3150	1165	1600	1375	——	800
		1130	1525	1330		685
			1505	1245		
(6) $[Cu(AsPh_3)_2(dbptH)I]$	3225	1110	1600	1325	——	765
			1515			
			1500			

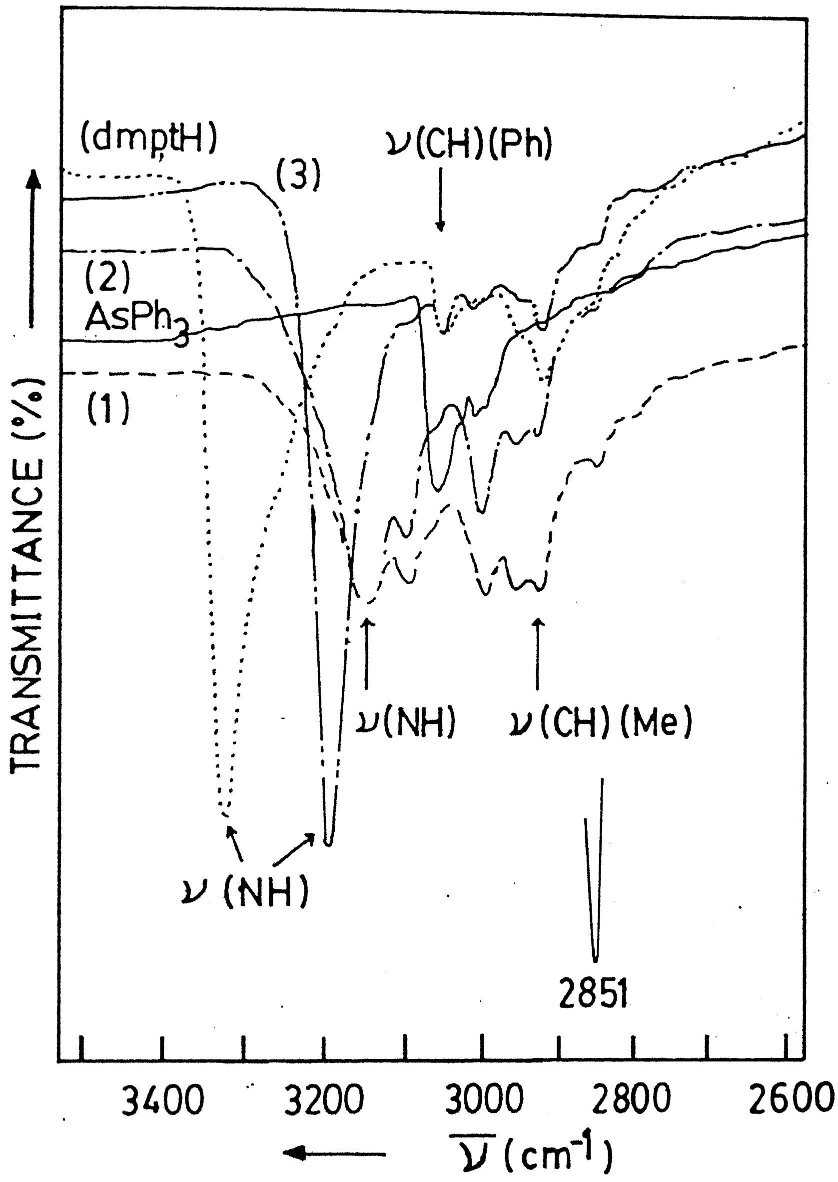

Figure 5.3. The expanded IR spectra of the ligands $AsPh_3$, dmptH and their complexes $[Cu(AsPh_3)_2(dmptH)Cl]$ (1), $[Cu(AsPh_3)_2$-$(dmptH)Br]$ (2) and $[Cu(AsPh_3)_2$-$(dmptH)I]$ (3) in the range 3500-2600 cm^{-1}, showing the shifting of $\nu(NH)$ band on hydrogen bonding.

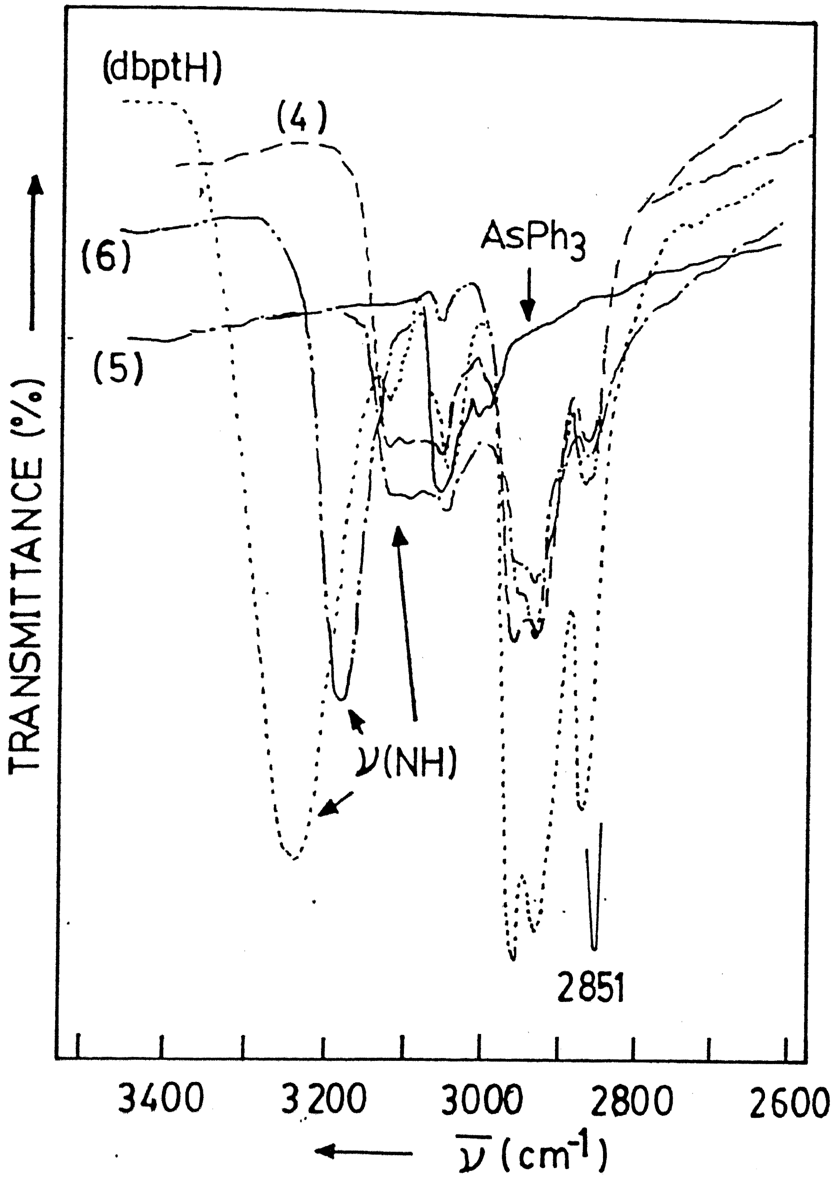

Figure 5.4. The expanded IR spectra of the ligands $AsPh_3$, dbptH and their complexes $[Cu(AsPh_3)_2(dbptH)Cl]$ (4), $[Cu(AsPh_3)_2$-$(dbptH)Br]$ (5) and $[Cu(AsPh_3)_2$-$(dbptH)I]$ (6) in the range 3500-2600 cm^{-1}, showing the shifting of ν(NH) band on hydrogen bonding.

These shifts indicate the involvement of C=S group in coordination. This is also supported by the red shift of the ν(C=S) band *ca* $\Delta\bar{\nu}$ = 25-30 cm^{-1} in case of the complexes of dmptH ligand, and the red shift or splitting of the ν(C=S) band of the complexes of dbptH ligand in which the red shifted bands are found to be intense. The bands observed at 770 and 710 cm^{-1} for the ligand dmptH, Figure 5.1, and at 765 and 715 cm^{-1} for the ligand dbptH, Figure 5.2, are assigned as thioamide band IV. The band at 770 cm^{-1} splits into two *ca* $\Delta\bar{\nu}$ = 35 cm^{-1} for the compound (**1**), Figure 5.1, and *ca* $\Delta\bar{\nu}$ = 30 cm^{-1} for the compound (**2**) but, for compound (**3**) the band is not discernible. The band at 710 cm^{-1} in the compounds is absent which may perhaps be coupled with the band due to phenyl groups at 695 cm^{-1} Figure 5.1. The band at 765 cm^{-1} of the dbptH ligand, Figure 5.2, splits into two bands *ca* 810 and 685 cm^{-1} or shifts to 685 cm^{-1} in all the three compounds (**4**), (**5**) and (**6**) and the band at 715 cm^{-1} is not observed in the complexes. All these observations clearly indicate the involvement of C=S group in the coordination. Bonding through sulphur atom is also favoured because copper(I), being soft acid, should prefer to interact with a soft base such as sulphur and indeed the presence of sulphur-copper(I) bond is confirmed by X-ray single crystal structure determinations of many complexes of ligands having thioamide group[245] and of

substituted thiourea ligands.[250] Specially Cu^{I}—S bond with heterocyclic thione donor ligands having thioamide group[29,106,66,68] has been extensively studied.

Four thioamide bands of the ligand tzdtH, I at 1490 cm^{-1}, II at 1245 cm^{-1}, III at 990 cm^{-1} and IV at 690 cm^{-1}, 650 cm^{-1} are assigned by Preti and Tosi[117] and they have reported various complexes including copper(I) with the deprotonated ligand. Vibrational analysis of the ligand has been done by Devillanova et al[231] who also reported the various copper(I) complexes[112] with the neutral ligand. The bands at 690 and 650 cm^{-1} which are assigned to ν(CS) *sym* and *asym* by Preti and Tosi[117] are assigned mainly due to Δ(NH) and $\nu(C_1S_1)$ (C_1 = carbon atom bonded with ring sulphur, S_1 = ring sulphur) respectively by Devillanova et al.[231] Keeping this difference of opinion in mind we have taken various other bands[231] to decide the coordination site.[117] The IR spectra of the free ligand tzdtH and its representative complex is given in Figure 5.5 and the major bands necessary for the assignments of the coordination site are collected in the Table 5.3. This ligand, tzdtH, is also bonded to the metal through the thione sulphur as shown by the shifts of the ν(CS) and ν(CN)+δ(NH) bands. The IR bands namely, ν(NH) at 3130 cm^{-1}, ν(CN)+δ(NH) at 1500 cm^{-1}, ν(CS) at 1085 cm^{-1} and 545 cm^{-1}, $\nu(CS_1)$+δ(CS)+ring def; (C = carbon atom bonded

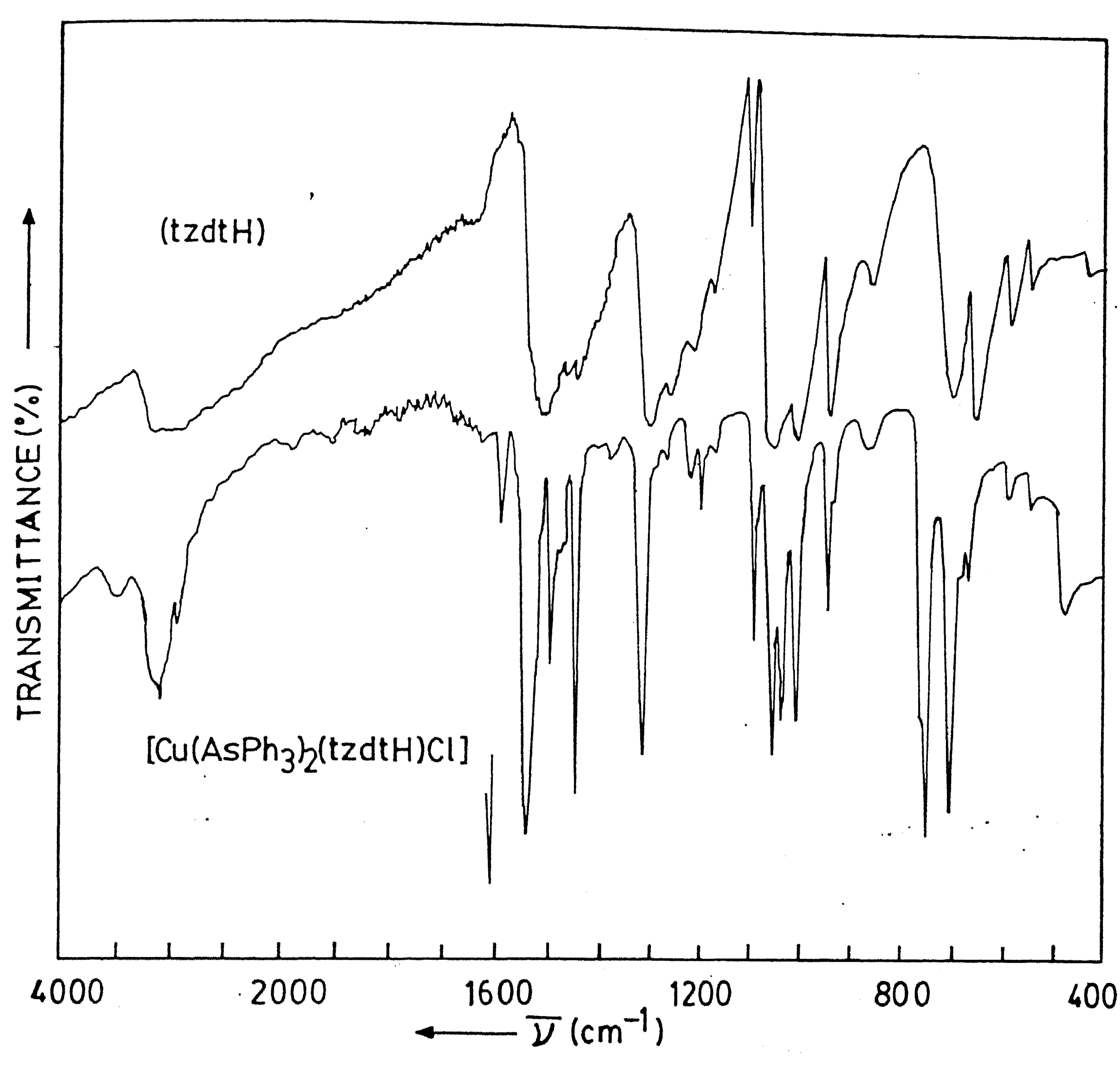

Figure 5.5. The IR spectra of the ligand tzdtH and its representative complex.

Table 5.3. Major IR bands of tzdtH and its complexes (cm^{-1})

Compound	$\nu(NH)$	$\nu(CN)+\delta(NH)$ ↓	$\nu(CS_1)$	$\nu(CS)$ ↓	$\Delta(CS)$	Vibrations between 600-400 cm^{-1}
Ligand (tzdtH)	3130-2700	1500	653 585	1085 545	434	585, 545, 434
(7) [$Cu(AsPh_3)_2$(tzdtH)Cl]	3125-3060	1535	660 585	1025 535	—	585, 535, 470
(8) [$Cu(AsPh_3)_2$(tzdtH)Br]	3130	1530	660 585	1025 530	—	580, 530, 465
(9) [$Cu(AsPh_3)_2$(tzdtH)I]	3160	1525	650 585	1025 530	—	580, 530, 465

with thione sulphur and ring sulphur) at 585 cm^{-1}, $\nu(C_1S_1)$+ring def at 653 cm^{-1} and Δ(CS) at 434 cm^{-1} of the free ligand,[231] Figure 5.5, are used to decide the donor site. Comparison of IR spectra of the free ligand with its complexes shows that ν(CS) bands at 1085 and 545 cm^{-1}, shifts to the lower frequency region, *ca* $\Delta\bar{\nu}$ = 60 and 10-15 cm^{-1} respectively. The Δ(CS) band at 435 cm^{-1} of the ligand is absent in the IR spectra of the complexes, Figure 5.5. This shows the major shift of the bands arising due to the C=S group which indicates the involvement of thione sulphur in the coordination. Other bands at 585, 653 and 1500 cm^{-1}, Figure 5.5, of the free ligand are observed either as such or shift towards the higher frequency region due to complex formation, which indicates the non-involvement of the ring sulphur and NH group. The ν(NH) band which shifts to the lower region may be due to hydrogen bonding. In fact very recently many copper(I) complexes of the triphenylarsine and the heterocyclic thione donors have been reported[68,73] of the same stoichiometry but with different heterocyclic thione donors and some of them have been characterized by single X-ray crystallography.

5.3.2 Electronic (UV-vis) and ^{1}H NMR Spectra

The electronic (UV-vis) spectra of the complexes and free ligands are given in Figures 5.6, 5.7, 5.8. The ^{1}H NMR

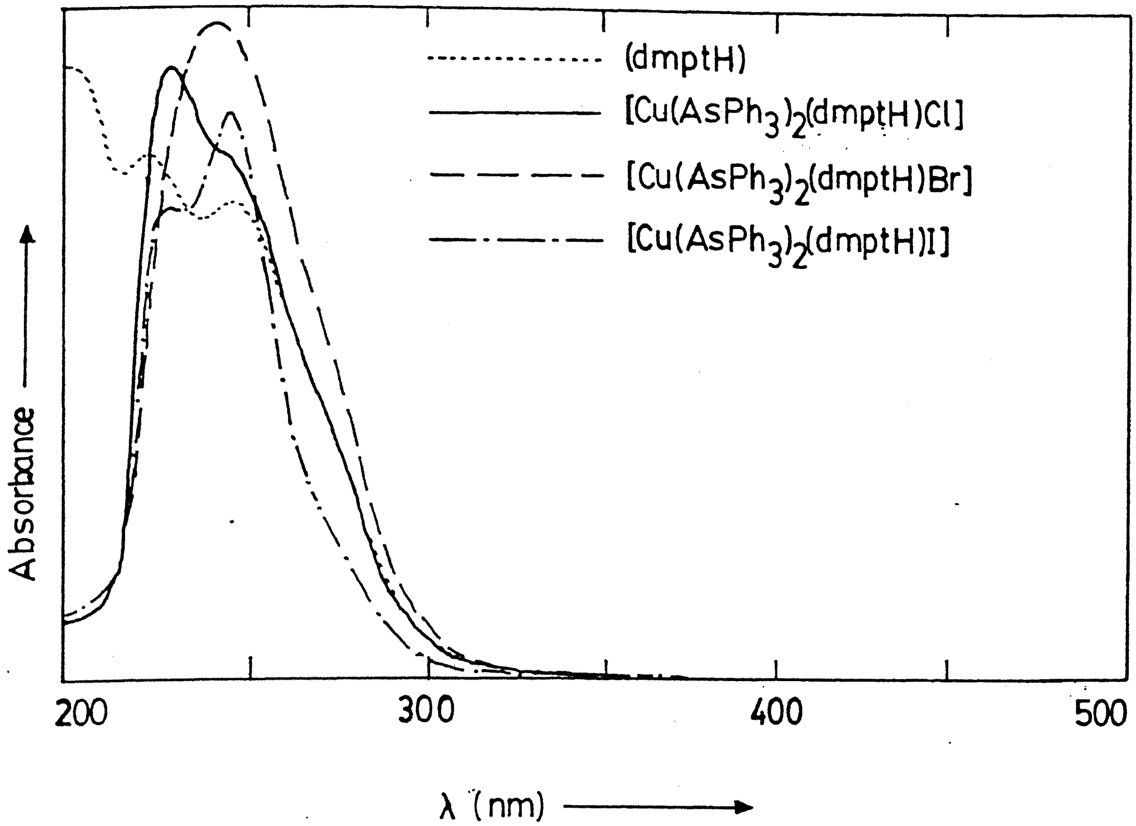

Figure 5.6. The electronic (UV-vis) spectra of the ligand dmptH and its complexes.

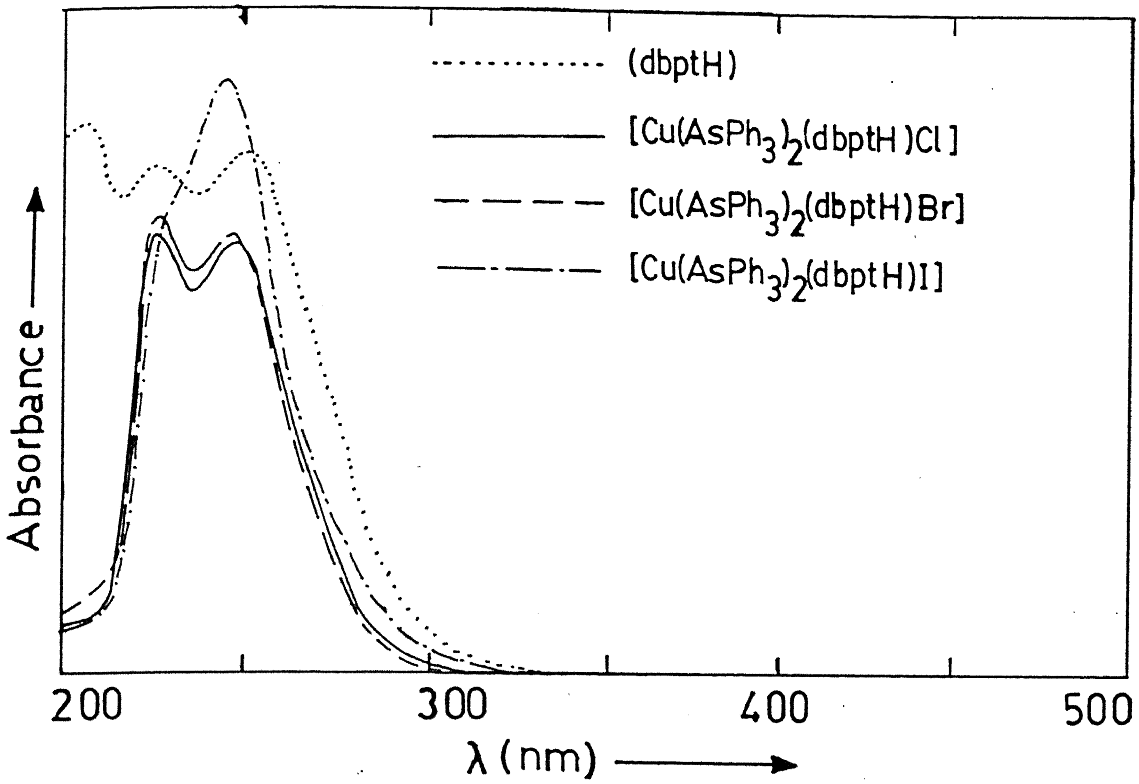

Figure 5.7. The electronic (UV-vis) spectra of the ligand dbptH and its complexes.

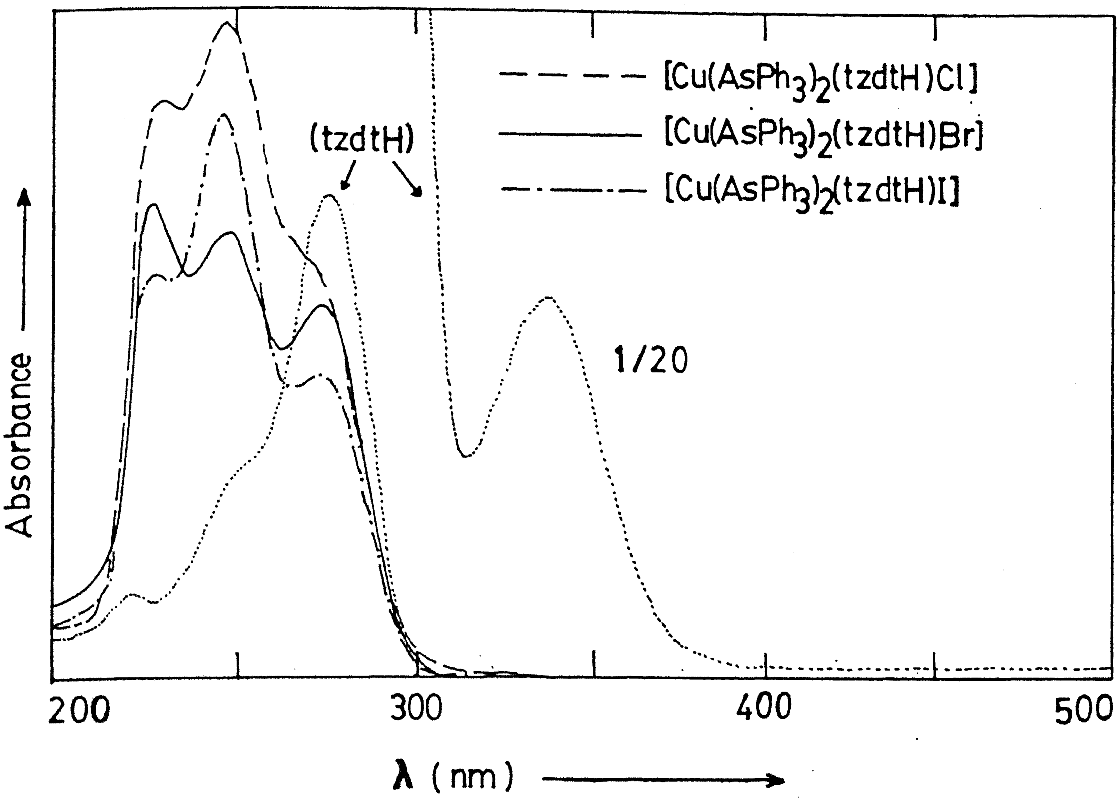

Figure 5.8. The electronic (UV-vis) spectra of the ligand tzdtH and its complexes.

spectra of the ligands and their representative complexes are given in Figures 5.9, 5.10, 5.11 and the electronic (UV-vis) and ^{1}H NMR data are collected in the Table 5.4 with assignments. As expected only UV absorption bands are observed which are assigned as intraligand (IL) transitions. The very weak band of the ligand tzdtH at 336 nm is not observed in its complexes, Figure 5.8. This band probably shifts to the higher energy region on complex formation. The ^{1}H NMR spectra of the complexes clearly show the peaks due to the ligands and triphenylarsines, Figures 5.9, 5.10, 5.11. The ^{1}H NMR signal of the >NH proton of the complexes appears as broad signal. The broadening of the signals may be due to hydrogen bonding.[29,73,68] The fine resolution ^{1}H NMR spectra at different concentration in the >NH region show almost no shift of the >NH proton signal which indicates the >NH hydrogens are intramolecularly bonded to the halides. The ^{1}H NMR spectra are recorded for the complexes after shaking the NMR solution with a few drops of D_2O. The peak due to >NH group was not found which confirms the presence of >NH group, its assignment and in turn the hydrogen bonding in the complexes. The gradual decrease in intramolecular hydrogen bonding strength is reflected by the corresponding lowering of δ values for >NH protons as one goes from chloride to bromide to iodide complexes.[68] The intramolecular hydrogen bonding of such

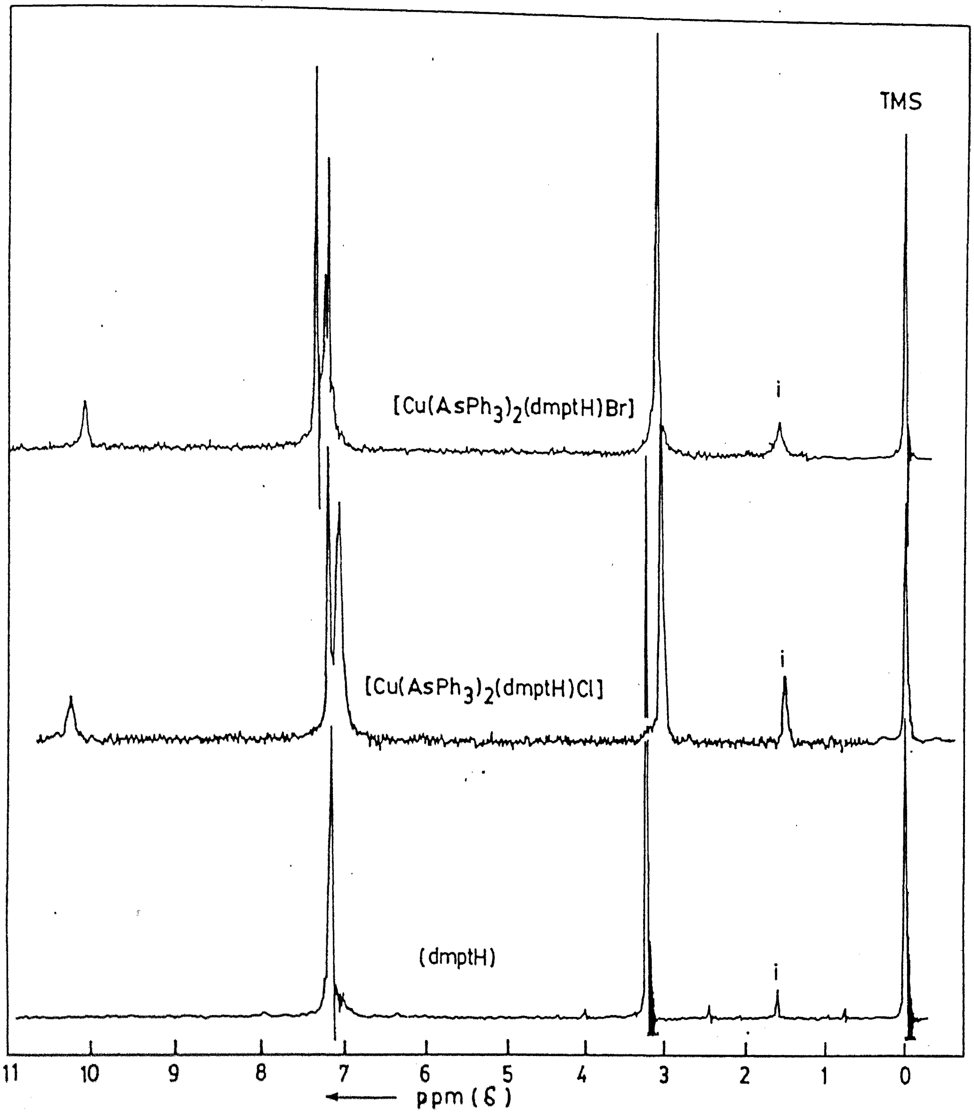

Figure 5.9. The ^{1}H NMR spectra of the ligand dmptH and its representative complexes. Peaks indicated by i are due to the impurity.

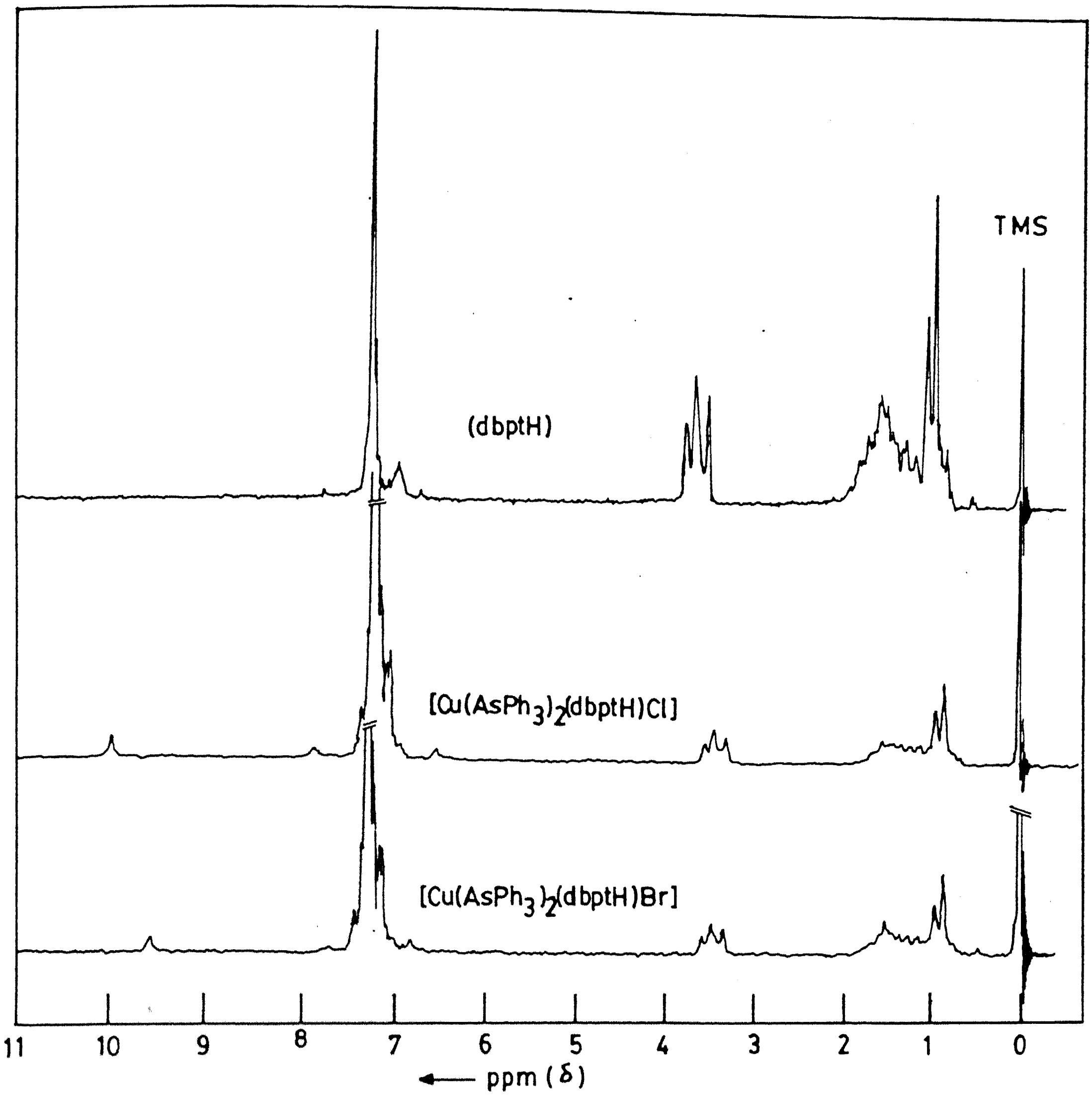

Figure 5.10. The ^{1}H NMR spectra of the ligand dbptH and its representative complexes.

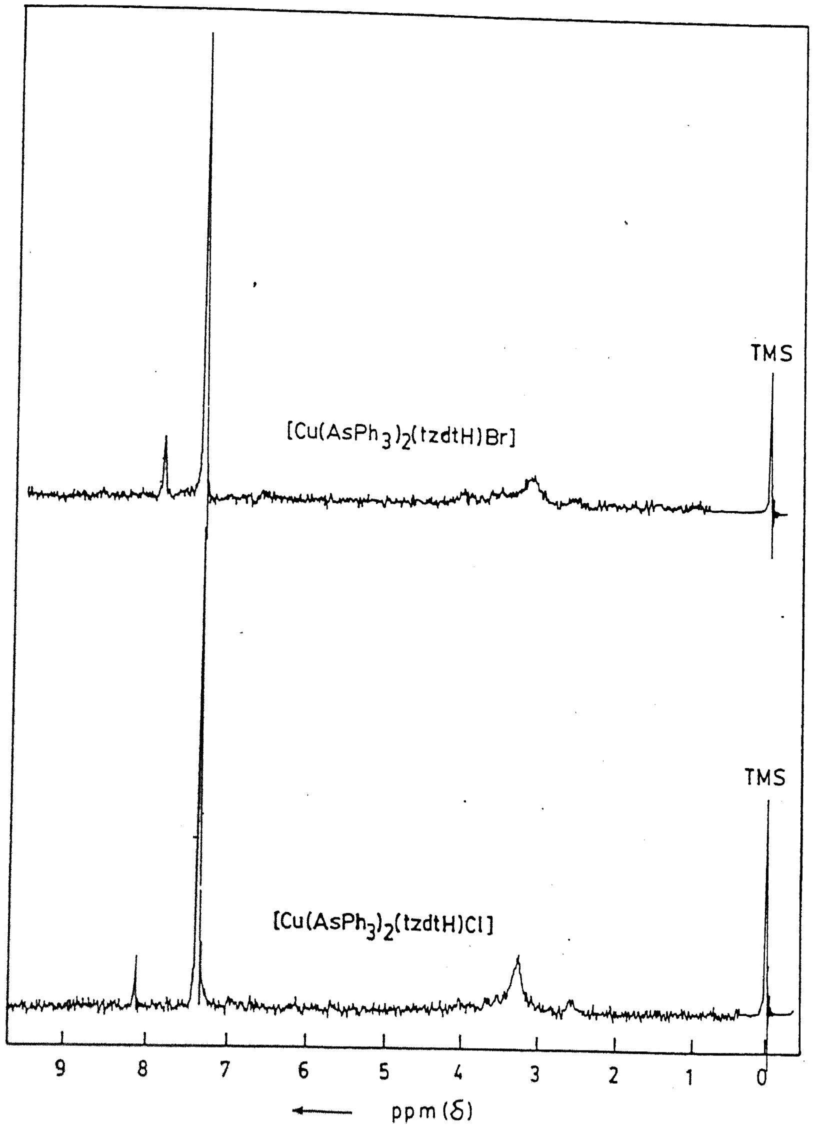

Figure 5.11. The ^{1}H NMR spectra of the representative complexes of ligand tzdtH.

Table 5.4. Electronic (UV-vis) spectral data of the ligands and the complexes in CH_3CN and ^1H NMR spectral data of the ligands and complexes in $CDCl_3$

Compound	Band Position, λ_{max}(nm) with Assignment	^1H NMR Signal with Assignments ppm(δ)
1	2	3
(dmptH)	223.0	3.27 (s, 6H, $-N(CH_3)_2$ group);
	246.5	7.20 (s, 5H, $-C_6H_5$ group).
(1) $[Cu(AsPh_3)_2(dmptH)Cl]$	228.0 IL	3.07 (s, 6H, $-N(CH_3)_2$ group);
		6.83-7.33 (m, 35H, $-C_6H_5$ groups);
		10.27(s, 1H >NH group).
(2) $[Cu(AsPh_3)_2(dmptH)Br]$	227.0 IL	3.7 (s, 6H, $-N(CH_3)_2$ group);
		6.83-7.33 (m, 35H, $-C_6H_5$ groups);
		9.93(s, 1H, >NH group).
(3) $[Cu(AsPh_3)_2(dmptH)I]$		3.10 (s, 6H, $-N(CH_3)_2$ group);
		7.00- 7.50 (m, 35H, $-C_6H_5$ groups);
		9.58(s, 1H, >NH group).
Ligand (dbptH)	207.0	0.67-2.00 (m, 6H, $-CH_3$ groups);
	225.0	3.63 (t, 12H, $>CH_2$ groups);
	251.0	6.67–7.33 (m, 35H, $-C_6H_5$ groups).
(4) $[Cu(AsPh_3)_2(dbptH)Cl]$	226.0 IL	0.67–1.83 (m, 6H, $-CH_3$ groups);
	247.0 IL	3.43 (t, 12H, $>CH_2$ groups);
		6.83–7.50 (m, 35H, $-C_6H_5$ groups);
		9.97(s, 1H, >NH group).

Table 5.4. (contd....)

1	2		3
(5) [$Cu(AsPh_3)_2$(dbptH)Br]	256.5	IL	0.67–1.83 (m, 6H, -CH_3 groups);
			3.50 (t, 12H, >CH_2 groups);
			7.00–7.67 (m, 35H, -C_6H_5 groups);
			9.53(s, 1H, >NH group).
(6) [$Cu(AsPh_3)_2$(dbptH)I]	211.5	IL	0.67–1.83 (m, 6H, -CH_3 groups);
	247.0	IL	3.53 (t, 12H, >CH_2 groups);
			6.83–7.40 (m, 35H, -C_6H_5 groups);
			9.07(s, 1H, >NH group).
Ligand [tzdtH]	276.0		3.27–4.17 (m, 4H, >CH_2 groups).
	221.0		7.97 (s[broad], 1H, >NH group).
	336.0		
(7) [$Cu(AsPh_3)_2$(tzdtH)Cl][a]	229.0	IL	2.50–4.00 (m, 4H, >CH_2 groups);
	247.0	IL	7.37 (s, 30H, -C_6H_5 groups);
			8.11 (s, 1H, >NH group).
(8) [$Cu(AsPh_3)_2$(tzdtH)Br][a]	215.0	IL	2.50-4.00 (m, 4H, >CH_2 groups);
	274.0	IL	7.37 (s, 30H, -C_6H_5 groups);
			7.84 (s, 1H, >NH group).
(9) [$Cu(AsPh_3)_2$(tzdtH)I][a]	248.0	IL	2.50–4.00 (m, 4H, >CH_2 groups);
	275.0	IL	7.37 (s, 30H, -C_6H_5 groups);
			7.50 (s, 1H, >NH group).

[a]The ^1H NMR spectra are recorded in dmso-d_6.

systems has also been confirmed by the X-ray crystallography.[68,73] On complexation the ^{1}H NMR signals of $>CH_2$ and $-CH_3$ groups shift slightly towards the higher magnetic field (lower δ value). The proportions of the protons, observed by integration are exactly matching with the proposed stoichiometry of the complexes.

5.4 SUMMARY

Reactions of CuX, $AsPh_3$ and the title ligands in the 1:4:1 ratio respectively yield $[Cu(AsPh_3)_2(LH)X]$. The complexes have been characterized on the basis of analytical, IR, electronic (UV-vis), ^{1}H NMR, conductivity and magnetic measurements. In all cases there is a distorted tetrahedral environment around copper(I) and the ligands (LH) bind through thione sulphur atom to copper(I).

CHAPTER 6*

CYANO-BRIDGED COPPER(I)-RUTHENIUM(II) COMPLEXES

6.1 INTRODUCTION

The design of suitable chromophores to be used as sensitizers in the photochemical conversion of solar energy is one of the goals of coordination chemists.[39,254,255] In this context ruthenium(II)-polypyridine complexes have attracted attention of many workers because of their excellent properties involving the role of light absorption and light emission sensitizer.[39] In recent years much work has been reported on cyano-bridged homo- and heteropolynuclear complexes,[182,54,56,256,207,257] to explore the various photophysical properties, including sensitization. Copper(I) a d^{10} system, is an electron rich centre and can be stabilized by the ligands having π-acidic character, viz PPh_3, bpy, phen, CO, CN^- *etc*. Extensive studies on copper(I) cyanide,[210]

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* R. Singh and S. K. Dikshit, *Polyhedron*, **1993** (in press).

cyanide-phosphine mixed-ligand complexes[212] and the phosphine-polypyridine complexes[124,258,259] have been carried out. There are some reports[54,204,260-264] on heteronuclear bimetallic cyanide bridged complexes containing ruthenium(II) and other metal centres, but, to the best of our knowledge, these are the first cyano-bridged heteronuclear bimetallic complexes containing copper(I) and ruthenium(II) metal centres. Since copper(I) complexes are known to show photophysical and photochemical properties,[5] it stimulated us to study the various aspects of copper(I)-ruthenium(II) dinuclear complexes. Our interests are four-fold: (a) to study the nature of stretching frequency of cyanide group when it is bridged between to two electron-rich metal centres, namely copper(I) and ruthenium(II), (b) how this cyanide bridging effects the electronic (UV-vis) and photophysical properties of the spectator ligands and the sub-units?, (c) to study the photoinduced intramolecular energy and electron transfer in the partially oxidized state, and (d) to study the electrochemical properties. In this chapter, we have described the syntheses, characterization and the study of IR stretching frequencies of cyanide group and the electronic (UV-Vis) spectral properties of these complexes. The studies of the photophysical and electrochemical properties of these complexes and their partially oxidized forms are under

investigation.

6.2 EXPERIMENTAL

6.2.1 Physical Methods

The carbon, hydrogen and nitrogen analyses, electronic (UV-vis), IR and ^{1}H NMR spectra, magnetic, conductivity and melting point measurements have been taken as described in previous chapter. But the expanded IR spectra have been taken on Perkin Elmer IR-841 double beam spectrophotometers as KBr pellet in the range of 2500-2000 cm^{-1} and the conductivity measurements have been carried out in nitrobenzene or acetonitrile solutions. The ^{13}C and ^{31}P NMR spectra have been recorded on Bruker WM-400 NMR spectrometer. For ^{31}P NMR spectra, 85% H_3PO_4 is used as an external calibrant whereas ^{13}C NMR peaks are relative to TMS (0 ppm).

6.2.2 Starting Materials

All the chemicals used are either of Analar or chemically pure grade. Invariably manipulations have been carried out under dry oxygen-free nitrogen using standard Schlenk line and other techniques.[265] The solvents have been dried by standard procedures[266] before use.

The complexes $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$,[159,160] and $[(bpy)_2\text{-}RuCl_2].2H_2O$[142] have been prepared according to the literature

procedures. A brief description of these methods is given below:

6.2.2(a) Preparation of $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$[159]

The reaction is carried out in a 2 L, two-neck, round-bottom flask equipped with a 500 mL dropping funnel and a reflux condenser topped with a nitrogen bypass. The apparatus is purged with nitrogen. Triphenylphosphine (21.0 g 0.08 mol) is dissolved in 1 L of ethanol by heating. (If the solution is not clear, it should be filtered before proceeding further.) Hydrated ruthenium trichloride (5.0 g 0.02 mol) is dissolved in ethanol (100 mL) by boiling and then allowing the solution to cool. Freshly distilled cyclopentadiene (10 mL, 8.0 g, 0.12 mol) is added to the ruthenium trichloride solution, and the mixture is transferred to the dropping funnel. The dark-brown solution is then added to the triphenylphosphine solution over a period of 10 minutes while maintaining the temperature at the reflux point. After the ruthenium trichloride/cyclopentadiene solution has been added, the mixture has a dark-brown colour, which after 1 hour has lightened to a dark red-orange. The solution, which can now be exposed to air, is filtered quickly while hot and cooled overnight at -10°C. Orange crystals separate, leaving a pale yellow-orange supernatant liquid. The crystals are collected on a sintered-glass filter, washed with ethanol (4 × 25 mL)

and with light petroleum ether (4 × 25 mL), and dried *in vacuo*. Yield *ca* 14 g, 90-95%.

The complex forms orange crystals melting point 130-133°C (decomposed) which are stable in air for prolonged periods. It is insoluble in light petroleum and water, slightly soluble in cold methanol or ethanol, diethyl ether, or cyclohexane, more soluble in chloroform, carbon tetrachloride, dichloromethane, carbon disulphide and acetone and highly soluble in benzene, acetonitrile, and nitromethane.

6.2.2(b) Preparation of *cis*-$[Ru(bpy)_2Cl_2]$[142]

Commercial $RuCl_3.3H_2O$ (7.8 g 29.8 mmol), 2,2′-bipyridine (9.36 g 60.0 mmol) and LiCl (8.4, 2 mmol) are heated at reflux in reagent grade dimethylformamide (50 mL) for 8 h. The reaction mixture is stirred magnetically throughout this period. After the reaction mixture has been cooled to room temperature, 250 mL of reagent grade acetone is added and the resultant solution is cooled at 0°C overnight. Filtering yielded a red to red-violet solution and dark green-black microcrystalline product. The solid is washed three times with 25 mL portions of water followed by three 25 mL portions of diethyl ether, and then it is dried by suction. Yields range from,65 to 70%.

6.2.3 Synthesis of Compounds

The cuprous cyanide,[63] and the complex $[Cu(PPh_3)_2CN]$[267]

are prepared by modifying the literature methods.

6.2.3(a) Cuprous Cyanide

In a warm (60°C) aqueous solution of $CuSO_4.5H_2O$ (2.5 g, 0.01 mol, 50 mL) with a constant bubbling of sulphur dioxide gas, a solution of an equivalent amount of sodium cyanide (0.49 g, 0.01 mol, 25 mL) in water is added with vigorous stirring. A precipitate immediately appears, which is filtered and washed thoroughly with water, ethanol and finally with ether and dried *in vacuo* over P_4O_{10} for several hours. The yield is almost quantitative.

6.2.3(b) Cyanobis(triphenylphosphine)copper(I) (1)

To a suspension of CuCN (0.01 mol) in benzene (50 mL) is added a solution of triphenylphosphine (0.04 mol) in benzene (70 mL) and the mixture is refluxed for 2 h. The clear solution thus obtained is cooled and filtered to remove any insoluble materials and the solvent is evaporated under reduced pressure. The residue is washed many times with ether to ensure the complete removal of excess triphenylphosphine. It is recrystallized from benzene/petroleum ether and dried *in vacuo*.

6.2.3(c) Cyano-2,2'-bipyridinetriphenylphosphinecopper(I) (2)

To a solution of $[Cu(PPh_3)_2CN]$ (1 mmol) in benzene (30 mL) is added a solution of 2,2'-bipyridine (1 mmol) in

benzene (30 mL) with constant stirring. The resulting yellow solution is refluxed for 1 h. The clear solution thus obtained is cooled, the volume is reduced to half under reduced pressure and the excess petroleum ether (60-80°C) (100 mL) is added, which results in the precipitation of pale yellow compound. It is separated by centrifugation and washed several times with petroleum ether and dried *in vacuo*.

6.2.3(d) Cyano-1,10-phenanthrolinetriphenylphosphinecopper(I)(3)

To a solution of [Cu(PPh_3)$_2$CN] (1 mmol) in benzene (30 mL) is added a solution of 1,10-phenanthroline (1 mmol) in benzene (30 mL) with constant stirring. Immediately an orange-red precipitate appears. This mixture is refluxed for half an hour. After cooling excess petroleum ether (60-80°C) (100 mL) is added to ensure the complete precipitation of the complex. The complex is centrifuged and washed several times with petroleum ether and dried *in vacuo*.

6.2.3(e) Bis(triphenylphosphine)copper(I)(μ-cyano)chlorobis(2,2'-bipyridine)ruthenium(II)hexafluorophosphate (4)

A mixture of [Cu(PPh_3)$_2$CN] (1 mmol) and [Ru(bpy)$_2$-Cl_2].$2H_2O$ (1 mmol) is suspended in ethanol (30 mL) and the suspension is refluxed for 1 h. An equal volume of water is then added and the solution is further refluxed for 1 h. The solution is cooled and filtered to remove any insoluble material present. To the filtrate is added a highly

concentrated solution of NH_4PF_6 in water (1 mL), which causes immediate precipitation of the complex. The precipitate is centrifuged and washed thoroughly with water and finally with ether and dried *in vacuo*.

6.2.3(f) Bis(triphenylphosphine)copper(I)(μ-cyano)cyclopentadienylbis(triphenylphosphine)ruthenium(II)hexafluorophosphate (5)

A mixture of $[Cu(PPh_3)_2CN]$ (1 mmol), $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ (1 mmol) and NH_4PF_6 (1.2 mmol) is suspended in methanol (60 mL) and refluxed for 1 h. During reflux all the $[(\eta^5\text{-Cp})\text{-}Ru(PPh_3)_2Cl]$ is dissolved and a pale yellow precipitate appears. The solvent is evaporated to dryness *in vacuo* and the residue is extracted with a small amount of dichloromethane and filtered. To the filtrate is added excess petroleum ether (100 mL) and the complex is precipitated, which is centrifuged and washed several times with petroleum ether and dried *in vacuo*.

6.2.3(g) Bis(triphenylphosphine)copper(I)(μ-cyano)cyclopentadienylbis(triphenylphosphine)ruthenium(II)tetrafluoroborate (6)

The procedure of the hexafluorophosphate is followed except $NaBF_4$ is used in place of NH_4PF_6.

6.2.3(h) 2,2'-Bipyridinetriphenylphosphinecopper(I)(μ-cyano)chlorobis(2,2'-bipyridine)ruthenium(II)hexafluorophosph

ate (7)

A mixture of [Cu(bpy)(PPh_3)CN] (0.2 mmol) and [Ru(bpy)$_2$-Cl_2].$2H_2O$ (0.2 mmol) in a 1:1 mixture of water and ethanol (50 mL), is suspended and refluxed for 3 h. The resulting solution is cooled and filtered to remove any insoluble material. To the filtrate is added a concentrated aqueous solution of NH_4PF_6 (1 mL). A precipitate immediately appears, which is centrifuged, washed several times with water and ether and dried over P_4O_{10} for several hours *in vacuo*.

6.2.3(i) 1,10-Phenanthrolinetriphenylphosphinecopper(I)(μ-cyano)chlorobis(2,2'-bipyridine)ruthenium(II)hexafluorophosphate (8)

The above procedure for the 2,2'-bipyridine analogue is followed, but in place of [Cu(bpy)(PPh_3)CN], its 1,10-phenanthroline analogue is used.

6.2.3(j) 2,2'-Bipyridinetriphenylphosphinecopper(I)(μ-cyano)cyclopentadienylbis(triphenylphosphine)ruthenium(II)hexafluorophosphate (9)

To a solution of [(η^5-Cp)Ru(PPh_3)$_2$Cl] (0.1 mmol) in methanol (30 mL) is added solid [(phen)Cu(PPh_3)CN] (0.1 mmol) and the mixture is refluxed for 2.5 h, whereby a clear solution is obtained. After cooling the reaction mixture is filtered to remove any insoluble material. To the filtrate is added a concentrated aqueous solution of NH_4PF_6 (2 mL) to

precipitate the complex. The complex obtained is centrifuged and washed several times with water and ether and dried *in vacuo* over P_4O_{10} for several hours.

6.2.3(k) 1,10-Phenanthrolinetriphenylphosphinecopper(I)(μ-cyano)cyclopentadienylbis(triphenylphosphine)ruthenium(II)hexafluorophosphate (10)

The above procedure for 2,2′-bipyridine analogue isfollowed using the 1,10-phenanthroline analogue in place of $[(bpy)Cu(PPh_3)CN]$.

6.3 RESULTS AND DISCUSSION

The analytical data for the complexes are given in Table 6.1, which are consistent with the stoichiometries proposed. Conductivity measurements have been performed in nitrobenzene or acetonitrile solutions. The conductivity data of the complexes (1), (2) and (3) show their non-electrolytic nature, where as the other cationic complexes are 1:1 electrolytes.[240] All the complexes are diamagnetic at room temperature.

6.3.1 IR Spectra

The IR spectra of the complexes are given in Figures 6.1, 6.2, and 6.3 and the expanded IR spectra of the complexes in the ν(CN) region are given in the Figures 6.4, 6.5, and 6.6. The ν(CN) stretching frequency of the complexes are given in

Table 6.1. Analytical and physical data of the complexes

	Compound	Colour	Analysis Found (calculated) (%) C	H	N	M.p.[a] (θ/°C)	Yield[b] (%)
(1)	$[Cu(PPh_3)_2CN]$	White	72.3 (72.4)	4.9 (5.0)	2.2 (2.3)	155	90
(2)	$[Cu(bpy)(PPh_3)CN]$	Yellow	68.5 (68.6)	4.6 (4.6)	8.0 (8.30	138	80
(3)	$[Cu(phen)(PPh_3)CN]$	Orange	56.6 (56.7)	3.9 (3.8)	6.0 (5.8)	198	92
(4)	$[(PPh_3)_2Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$	Orange-red	64.5 (64.6)	4.7 (4.5)	1.1 (1.0)	218d	84
(5)	$[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$	Yellowish-white	64.5 (64.6)	4.7 (4.5)	1.1 (1.0)	222d	70
(6)	$[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]BF_4$	Pale-yellow	67.2 (67.3)	4.6 (4.7)	0.9 (0.9)	130	80
(7)	$[(bpy)(PPh_3)Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$	Maroon	43.6 (43.4)	3.4 (3.6)	9.0 (8.9)	173d	80
(8)	$[(bpy)(PPh_3)Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$	Yellowish-white	62.4 (62.6)	4.5 (4.4)	2.9 (3.1)	130d	40
(9)	$[(phen)(PPh_3)Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$	Orange-red	54.2 (54.4)	3.5 (3.7)	8.8 (8.7)	185d	85
(10)	$[(phen)(PPh_3)Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$	Yellow	63.0 (63.2)	4.5 (4.4)	3.4 (3.1)	128d	60

[a]d indicates the decomposition. [b]Based on copper for compounds (1), (2), (3), and on ruthenium for the rest of the compounds.

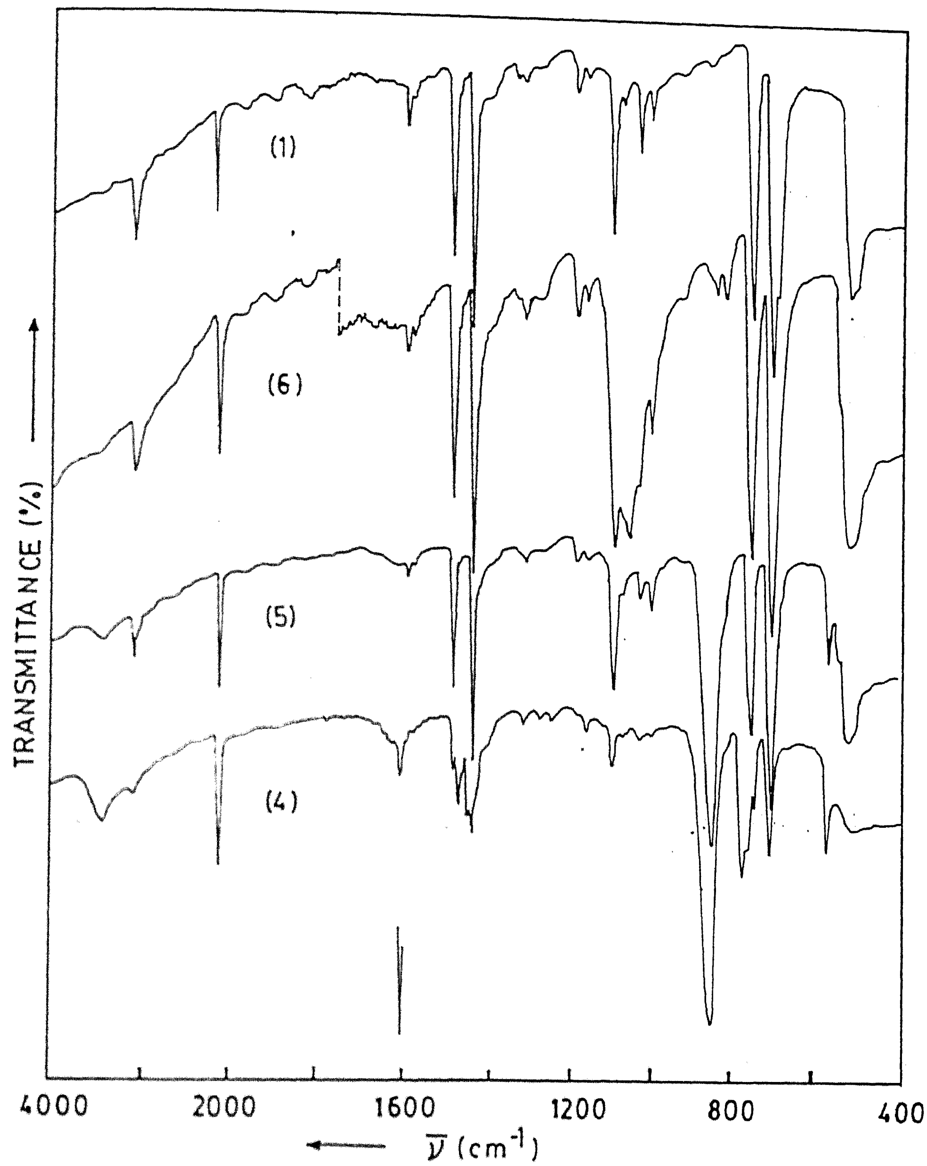

Figure 6.1. The IR spectra of the complexes $[Cu(PPh_3)_2CN]$ (1), $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$ (4), $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$ (5) and $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]BF_4$ (6).

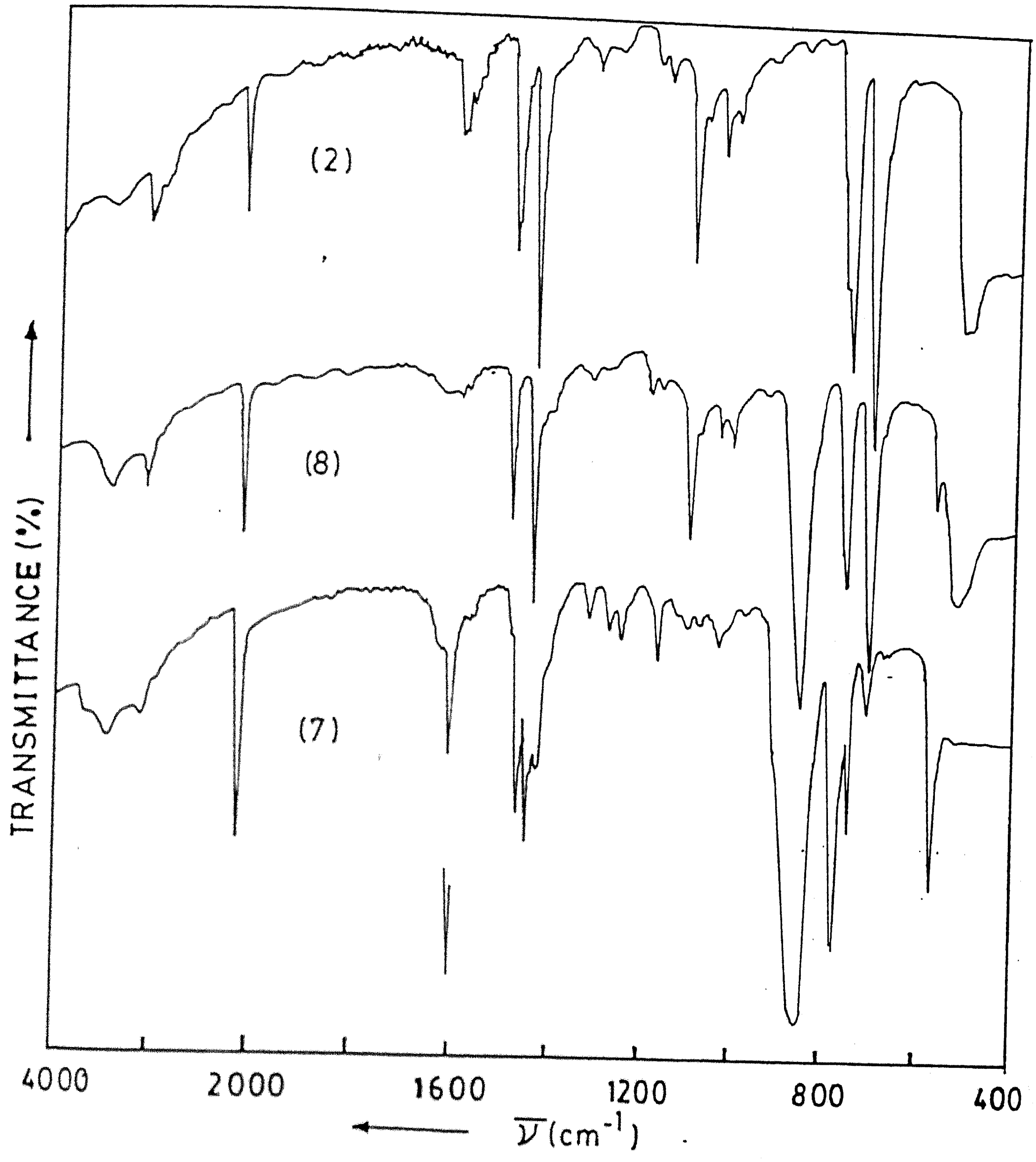

Figure 6.2. The IR spectra of the complexes $[Cu(bpy)(PPh_3)CN]$ (2), $[(bpy)(PPh_3)Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$ (7) and $[(bpy)(PPh_3)Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$ (8).

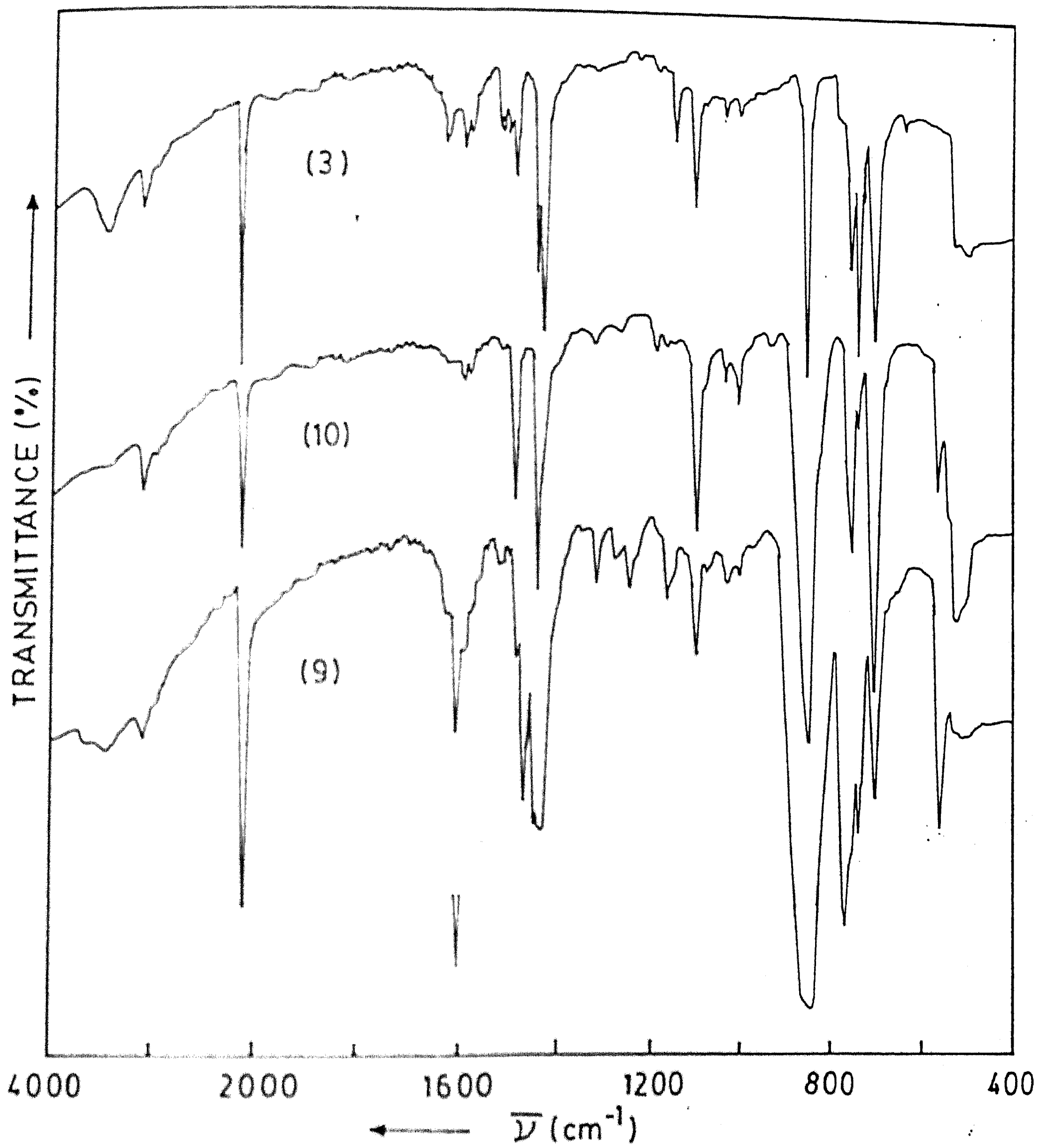

Figure 6.3. The IR spectra of the complexes [Cu(phen)(PPh_3)CN] (**3**), [(phen)(PPh_3)Cu(μ-CN)Ru(bpy)$_2$Cl]PF_6 (**9**) and [(phen)(PPh_3)Cu(μ-CN)Ru(η^5-Cp)(PPh_3)$_2$]PF_6 (**10**).

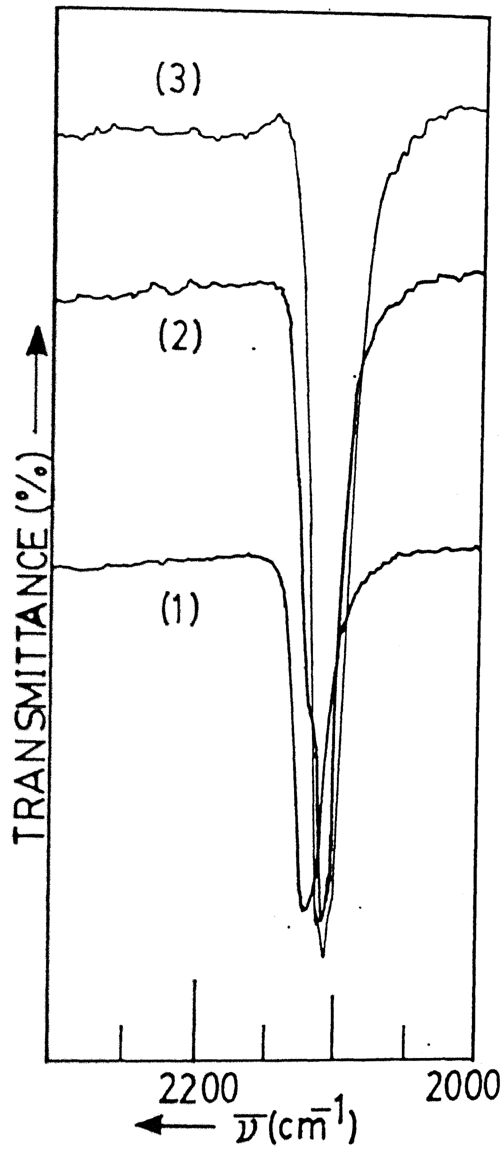

Figure 6.4. The expanded IR spectra of the complexes $[Cu(PPh_3)_2CN]$ (**1**), $[Cu(bpy)(PPh_3)CN]$ (**2**) and $[Cu(phen)(PPh_3)CN]$ (**3**) in the region 2300-2000 cm^{-1}.

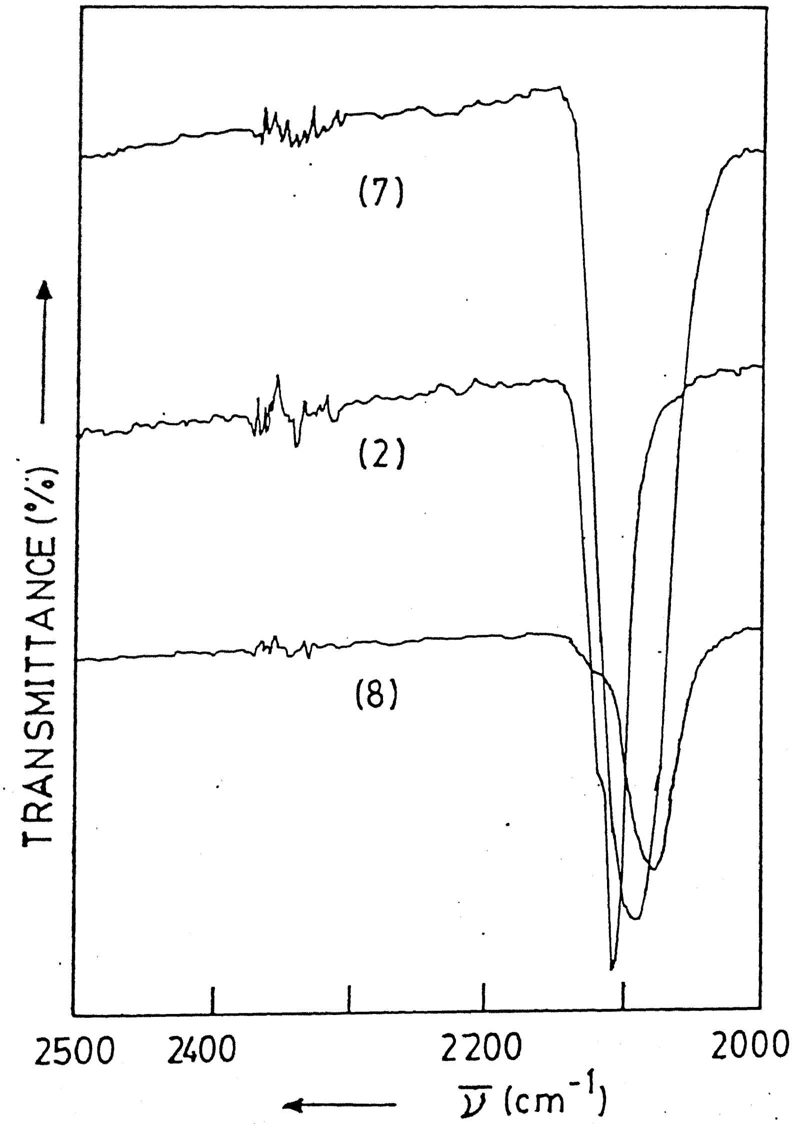

Figure 6.5. The expanded IR spectra of the complexes $[Cu(bpy)(PPh_3)CN]$ (2), $[(bpy)(PPh_3)Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$ (7) and $[(bpy)(PPh_3)Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$ (8) in the region 2500-2000 cm^{-1}.

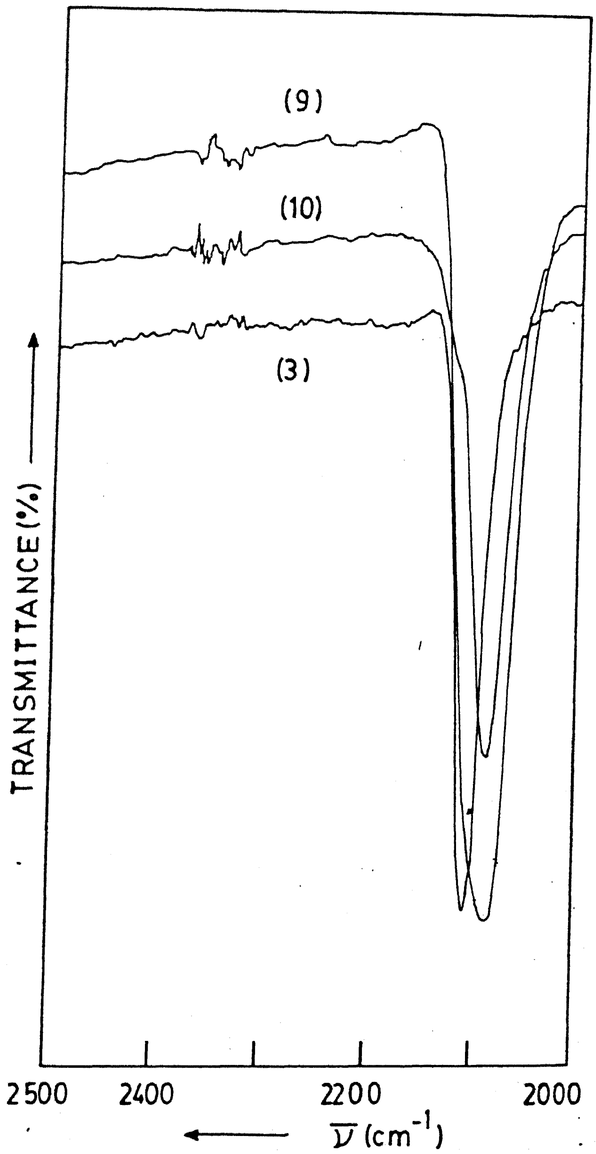

Figure 6.6. The expanded IR spectra of the complexes [Cu(phen)(PPh_3)CN] (3), [(phen)(PPh_3)Cu(μ-CN)Ru$(bpy)_2$Cl]PF_6 (9) and [(phen)(PPh_3)Cu(μ-CN)Ru(η^5-Cp)$(PPh_3)_2$]PF_6 (10) in the region 2500-2000 cm^{-1}.

Table 6.2. The ν(CN) band of $[Cu(PPh_3)_2CN]$ occurs at 2121 cm^{-1} (lit.,[120] 2105 cm^{-1}). In solid cuprous cyanide ν(CN) occurs[220,268,269,223] at 2172 cm^{-1}. Red shift of *ca* 51 cm^{-1} indicates that CN group is coordinated to $(PPh_3)_2Cu$ moiety. In addition, copper(I) is an electron rich centre which is also bonded to triphenylphosphine, a stronger σ-donor than π-acceptor, therefore a strong back donation from Cu(I) to cyanide group is expected, which may also be contributing to the red shift of ν(CN) in $[Cu(PPh_3)_2CN]$. There is a small red shift of ν(CN) in $[Cu(bpy)(PPh_3)CN]$ (*ca* $\Delta\bar{\nu}$ = 13 cm^{-1}) and in $[Cu(phen)(PPh_3)CN]$ (*ca* $\Delta\bar{\nu}$ = 15 cm^{-1}) compared with ν(CN) of $[Cu(PPh_3)_2CN]$, Figure 6.4, which is in accordance with the analogy that, as the coordination number increases, the net positive charge on the metal centre decreases and in turn the σ-bonding from cyanide group decreases, resulting in decrease of ν(CN).[209]

In general the bridging cyanide group gives the stretching band at higher wave number[209] than the terminal cyanide group. The shifting of ν(CN) group to the higher region on bridging, has been explained on the basis of force field arguments.[220] However, this is not always the case and the band position of the cyanide group depends upon many other factors. The ^{13}C and ^{15}N NMR and IR studies[222] of cyano (ligand) cobaloximes have furnished evidence for cobalt(I)-to-cyanide

Table 6.2. The spectral data of the complexes

Compounds	UV-Vis bands[a] λ_{max}(nm)	Assignment	ν(CN) (cm^{-1})	^{1}H NMR signal[c] of Cp ppm(δ)	^{13}C NMR signal[c,d] ppm(δ)	^{31}P NMR signal ppm(δ)
(1)	236.0	IL	2121		128-135 (m, $-C_6H_5$ groups) 151.9 (s(broad), CN)	-2.6 (s, Cu-P)
	259.5	CT				
(2)	261.0sh	CT	2108			
(3)	268.0	CT	2106			
(4)	244.0	$\pi^* \longleftarrow \pi$(bpy) IL	2087			
	291.0	$\pi^* \longleftarrow \pi$(bpy) IL				
	340.0	π_2^*(bpy) $\longleftarrow d\pi$(Ru) CT				
	475.0	π^*(bpy) $\longleftarrow d\pi$(Ru) CT				
(5)	228.0	IL	2075	4.23		
	268.0sh	CT				
(6)	229.0	IL	2084	4.33	85.6 (s, Cp); 128-138 (m, $-C_6H_5$ groups)	-3.4 (s, Cu-P) 48.9 (s, Ru-P)
	269.0sh	CT				
(7)	244.0	$\pi^* \longleftarrow \pi$(bpy) IL	2091			
	287.0	$\pi^* \longleftarrow \pi$(bpy) IL				
	345.0	π_2^*(bpy) $\longleftarrow d\pi$(Ru) CT				
	471.0	π^*(bpy) $\longleftarrow d\pi$(Ru) CT				
(8)	270.0	CT	2079	4.27		
(9)	244.0	$\pi^* \longleftarrow \pi$(bpy) IL	2087			
	291.0	$\pi^* \longleftarrow \pi$(bpy) IL				
	344.0	π_2^*(bpy) $\longleftarrow d\pi$(Ru) CT				
	478.0	π^*(bpy) $\longleftarrow d\pi$(Ru) CT				
(10)	267.0	CT	2085	4.37		

[a]In acetonitrile solution, sh denotes shoulder. [b]In KBr disc. [c]In $CDCl_3$. [d]The ^{13}C NMR signals of the cyano group were not observed.

π-bonding. The ν(CN) tends to decrease with increasing basicity of the ligand *trans* to CN^-. Strong bases make cobalt(I) richer in electron density, resulting in increased back bonding to π^* of CN^- causes a decrease in ν(CN). The complexes, reported here, also show a red shift and broadening of ν(CN) on bridging. Both copper(I) and ruthenium(II) centres are electron rich and are also bonded to strong σ-donor and poor π-acid ligand triphenylphosphine and/or electron rich ligands. Lowering of ν(CN) stretching frequency on bridging may be because of enhanced π-back donation from ruthenium(II) and copper(I) to the π^*-orbitals of the cyanide group. All the characteristic bands due to the other ligands namely triphenylphosphine, 2,2′-bipyridine and 1,10-phenanthroline, are found in their spectral region, Figures 6.1, 6.2, 6.3. The characteristic vibrational frequency due to Cp is completely masked by the strong broad characteristic peak of PF_6^- in the complexes having this group, but the presence of the Cp group in the respective complexes is evident by the NMR signal of Cp group.

6.3.2 The ^{1}H NMR Chemical Shifts

The ^{1}H NMR data are collected in Table 6.2. Complexes having the Cp group show a sharp singlet signal in the range 4.1-4.4 ppm(δ), Figure 6.7, which is diagnostic. The Cp peak of the complexes shifts slightly to higher δ (low field) in comparison to the parent complex $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$. The

shifting of the Cp proton signal to the higher δ (low field) on coordination through the nitrogen atom of the CN group is consistent with the literature reported observation.[56,165,156] The high δ value of the Cp protons in these complexes also suggest that the complexes must be cationic in nature.[56,259] The proton signals of the phenyl groups and of the bpy and phen ligands appear in the region of 7.0-8.0 ppm(δ) as broad multiplets, Figure 6.7.

6.3.3 The ^{13}C and ^{31}P NMR Chemical Shifts

The ^{13}C and ^{31}P NMR data of the compound (1) and (6) are collected in Table 6.2, and the spectra are shown in Figures 6.8 and 6.9 respectively. All the peaks in the ^{13}C NMR spectra are found in the expected region of phenyl group[78,170] and cyanide group[219,270,271] for the compound (1). However, the ^{13}C NMR peaks due to the phenyl groups associated with copper(I) and ruthenium(II) metal centres for the compound (6) become too complicated to be assigned properly, Figure 6.8. The distinct ^{13}C NMR peak at 85.6 ppm(δ) is due to the cyclopentadienyl group, which is in the expected region.[166-169] The ^{13}C NMR signal due to the CN group is not observed. However, the presence of CN group in the complexes is evident by the strong ν(CN) band in the IR spectra. The compound (1) shows only one ^{31}P NMR signal at -2.6 ppm(δ) which is at lower field relative to the free triphenylphos-

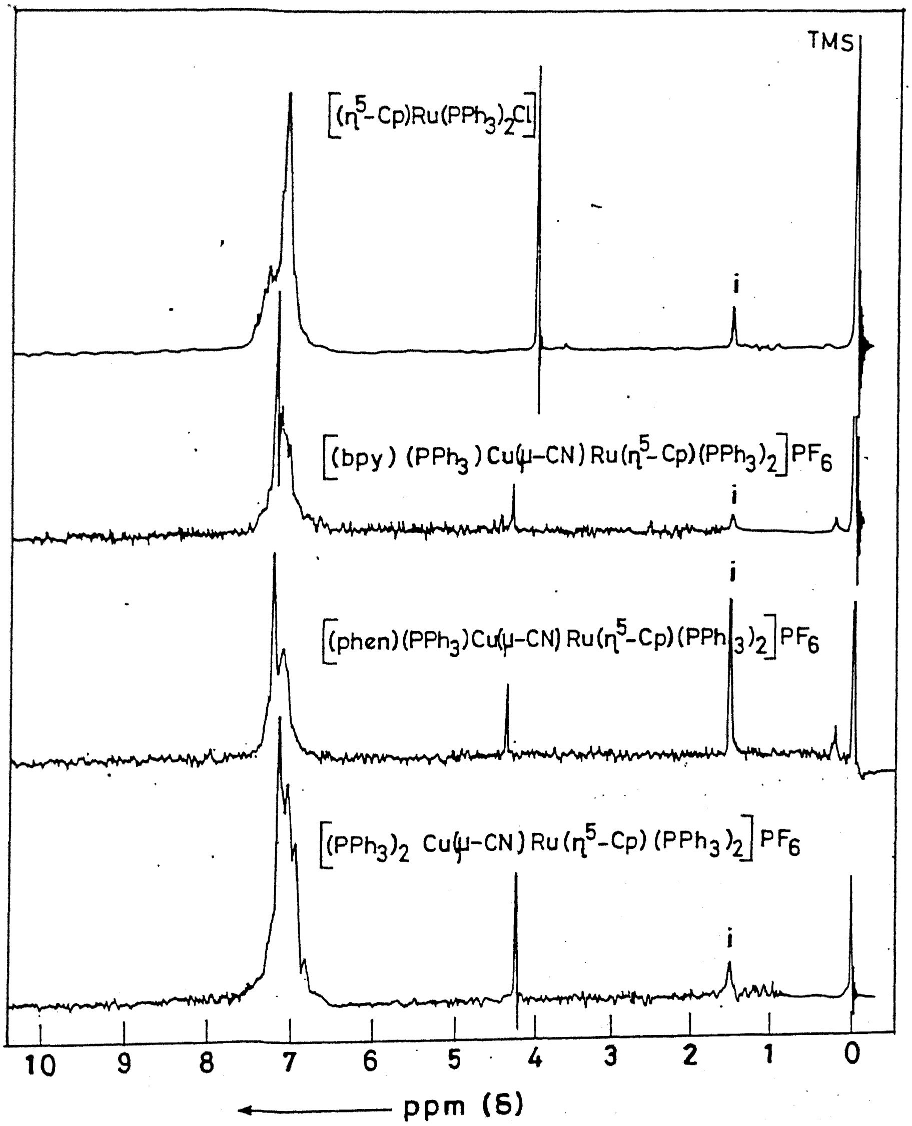

Figure 6.7. The ^{1}H NMR spectra of the complexes containg Cp group. The peaks indi cated by i are due to impurtity.

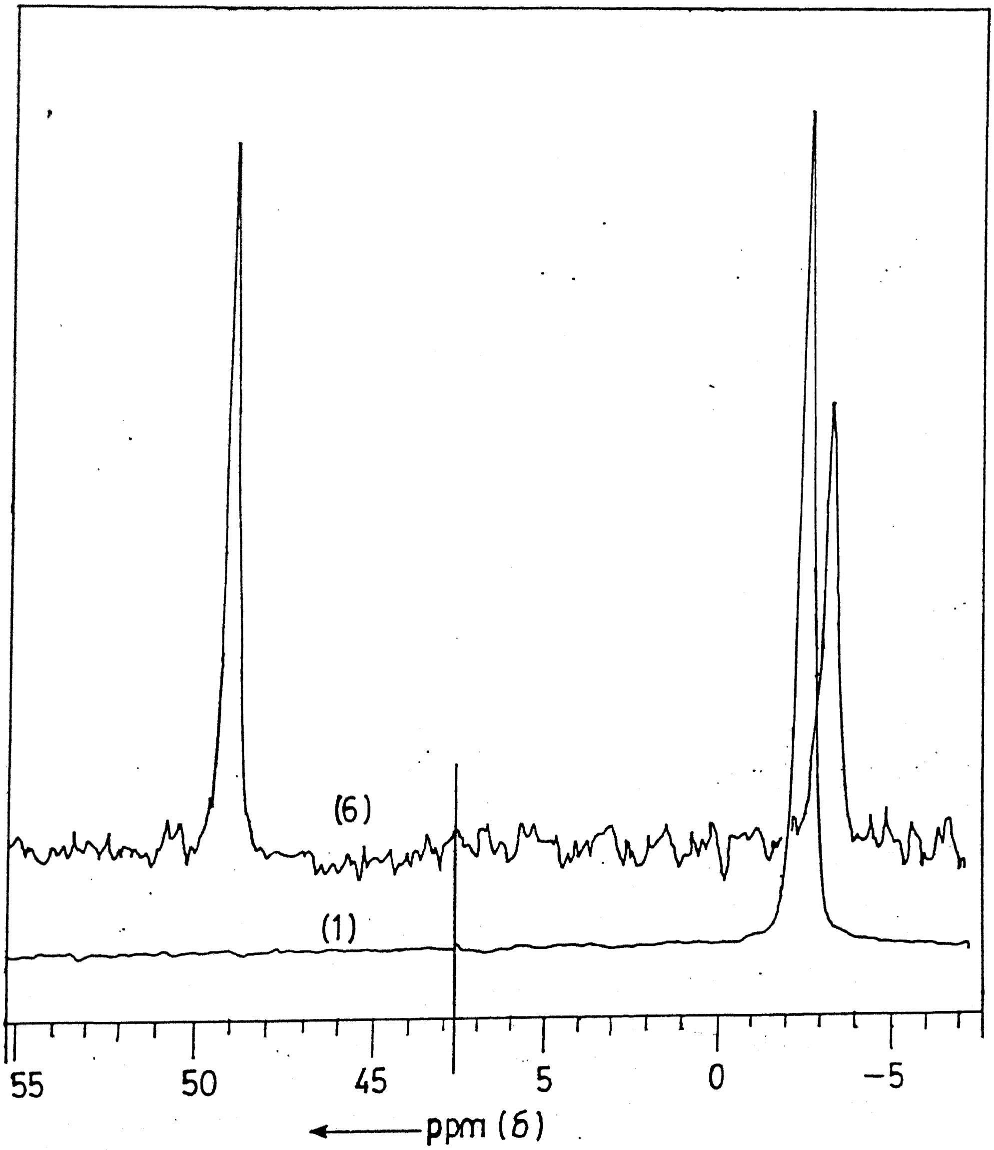

Figure 6.9. The ^{31}P NMR spectra of the complexes $[Cu(PPh_3)_2CN]$ (1) and $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]BF_4$ (6).

phine ^{31}P NMR signal[78] at -6.00 ppm(δ). This is expected as the formation of the complex (1) causes deshielding of the phosphorus nuclei, because of the shifting of electron density from the phosphorus atom to copper(I) metal centre, which is in accordance with the greater σ-donation than the π-accepting properties of the triphenylphosphine ligand. The dinuclear complex (6) as expected shows two ^{31}P NMR signals at 48.9 and -3.4 ppm(δ) which are assigned for the phosphorus atoms of the triphenylphosphine ligands associated with ruthenium[172] and copper metal centres, respectively. The ^{31}P NMR signal in the compound (6), at -3.4 ppm(δ) due to the copper sub-unit, is at higher field (lower δ value) in comparison with the compound (1), Figure 6.9, and at lower field (higher δ value) than the free triphenylphosphine. This arises from competitive π-back donation to cyanide from copper(I) and ruthenium(II) metal centres. Due to π-back acceptance from ruthenium(II), there is a concomitant decrease in π-interaction with copper(I) and thereby enhanced probability of electron availability on copper(I) for Cu—P π-back bonding. This results in the shielding of phosphorus nuclei of triphenylphosphine of the copper sub-unit and, therefore, shifting of the ^{31}P NMR signal to the high field (lower δ value), Figure 6.9. The trends indicate that shifting of electron density from a ruthenium centre to cyanide group may cause the deshielding of the

phosphorus nuclei associated with the ruthenium sub-unit and hence shifting of the ^{31}P NMR signal to the lower field (higher δ value). In fact the ^{31}P signal of the ruthenium sub-unit is observed at 48.9 ppm(δ), which is much higher in comparison to the parent compound $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ (lit.,[165] 38.6 ppm), which supports the discussed trend of the shifting of ^{31}P NMR signals and ruthenium to cyanide group π-back bonding.

6.3.4 Electronic (UV-Vis) Properties

Data of the electronic (UV-vis) spectra are given in Table 6.2, and the spectra are shown in Figures 6.10 and 6.11. In the electronic absorption spectra of complexes (4) and (9), four peaks and a shoulder at 244 nm are observed, Figure 6.11. These bands are denoted as I to V in order of increasing energy, Figure 6.10. These are characteristic bands of the $Ru(bpy)_2^{2+}$ chromophore.[142,149,150] Assignments of these bands are given in Table 6.2. In all the complexes having this chromophoric group, band III, which is assigned as $\pi^* \longleftarrow \pi(bpy)$ intraligand transition has very slightly shifted to the higher energy in comparison to the parent complex $[Ru(bpy)_2Cl_2].2H_2O$. Assignments of bands I $[\pi^*_{bpy} \longleftarrow d\pi(Ru)]$ and II $[\pi^*_{bpy} \longleftarrow d\pi(Ru)]$ as charge transfer transitions is based on literature reports.[142,149,150] In these complexes, due to the strong back bonding from ruthenium(II) to the cyanide group, both the

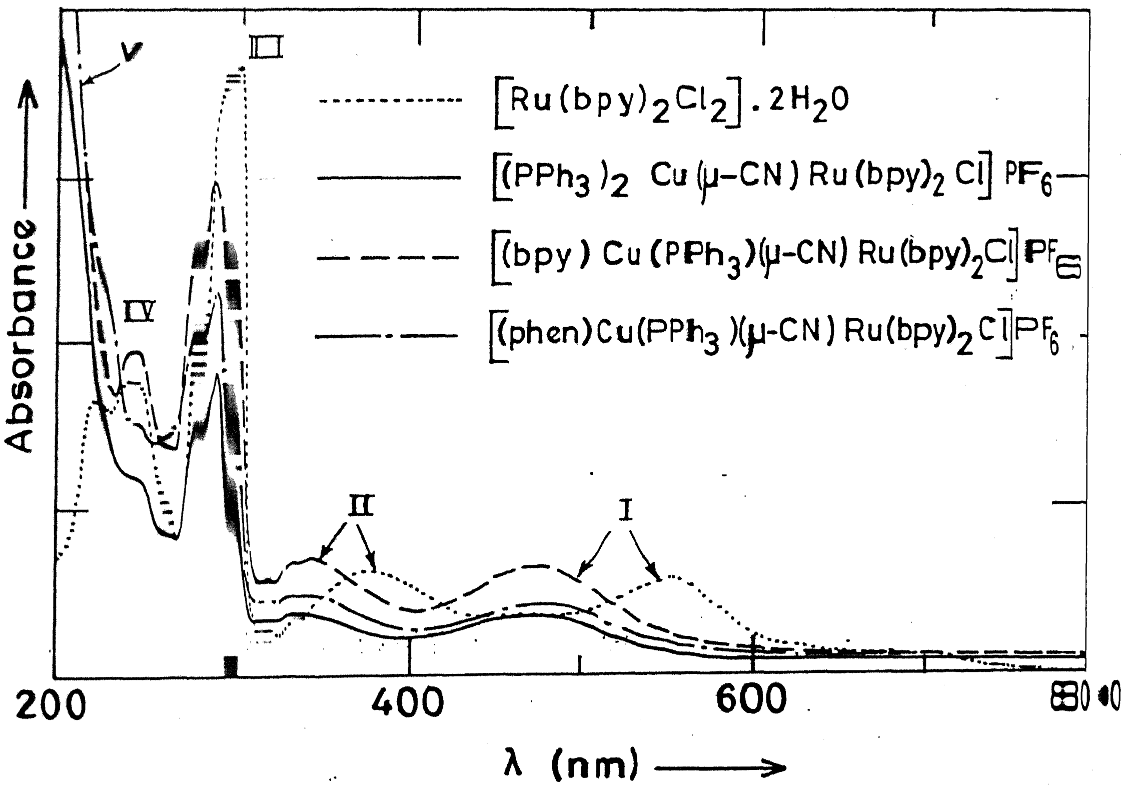

Figure 6.10. The electronic (UV-vis) spectra of the complexes containing $[Ru(bpy)_2Cl]^+$ unit.

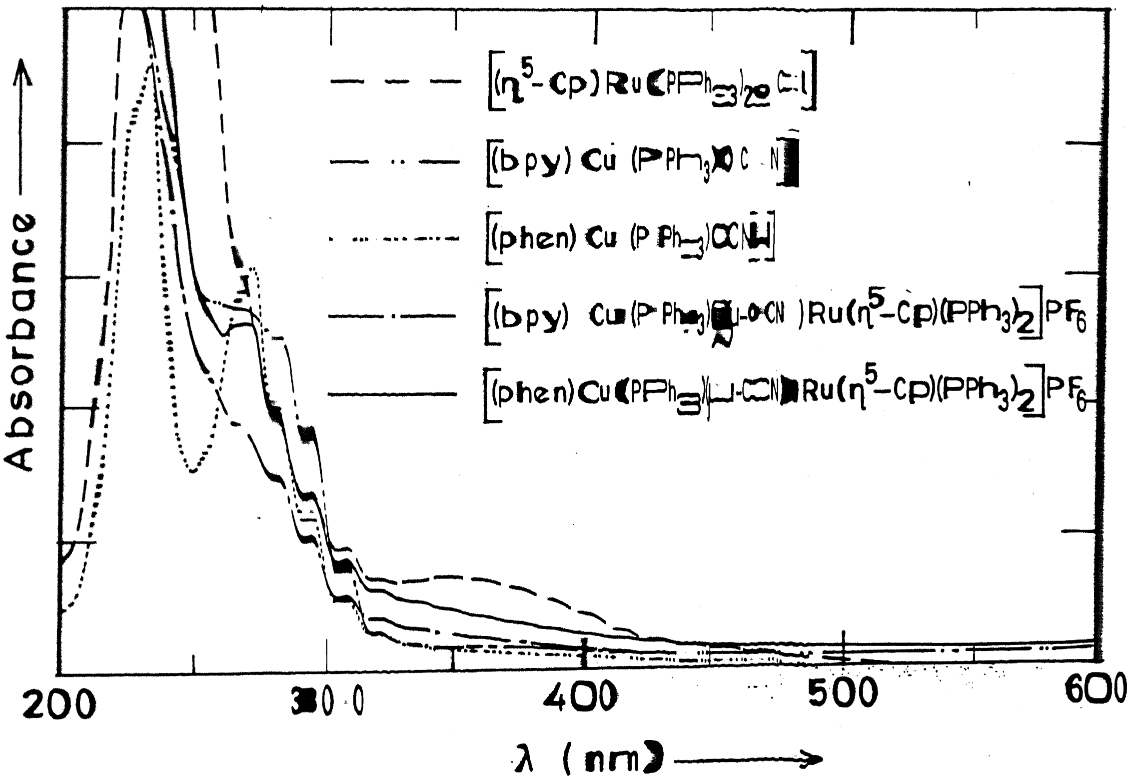

Figure 6.11. The electronic (UV-vis) spectra of the complexes containing Cp group, [Cu(bpy)(PPh_3)CN] (2) and [Cu(phen)(PPh_3)CN] (3).

bands I and II move to higher energies, Figure 6.10. This behaviour is expected if the *d*-orbitals are increasingly stabilized because of enhanced back bonding from ruthenium(II) to the cyanide group. In this context, the $\pi^*(\text{bpy}) \longleftarrow d\pi(\text{Ru})$ transitions act as spectator transitions for the CN——Ru interactions. This indicates the strong back bonding from ruthenium(II) to the cyanide group, which is also evident from shifting of the $\nu(\text{CN})$ stretching frequency to the lower energy region. Band IV appears as shoulder on band V, and can be assigned to intraligand $\pi^* \longleftarrow \pi(\text{bpy})$ transition[142,150] or, where aromatic phosphines are present, to a mixture of $\pi(\text{bpy})-\pi^*(\text{bpy})$ and $\pi(\text{phenyl})-\pi^*(\text{phenyl})$ transitions.[142] It is clearly seen in the absorption spectrum of the complex (7), as this complex has relatively less PPh_3 and more bpy group, it shows a well resolved peak of band IV at 244 nm, Figure 6.10. Complexes (1), (2) and (3) give absorption bands at 259.5, 268 and 261 nm (shoulder), respectively, which are assigned as MLCT transitions and the other bands in higher energy region are assigned as $\pi^* \longleftarrow \pi$ intraligand (IL) transitions. The band at 259.5 nm of complex (1) appears as a shoulder on band III of compound (4) at 280 nm. Similarly the band at 268 nm of complex (3), appears as shoulder on band III of the complex (9) at 270 nm. On the other hand in the case of the complex (7), because its band III occurs reasonably at higher energy

(287 nm) region there is mixing of the band at 261 nm of compound (2) and no shoulder is observed. The higher energy IL bands of the complexes (1), (2) and (3) are mixed with a $\pi^* \longleftarrow \pi$ (IL) bands at 222 nm of the bpy ligand and appear as band V in the complexes (4), (7) and (9). The absorption spectra of the compounds (2), (3), (8) and (10) are given in Figure 6.11. The MLCT transition at 349 nm of the complex $[(\eta^5\text{–Cp})Ru(PPh_3)_2Cl]$ is shifted to the higher energy region on the formation of the bridged complexes (8) and (10), and becomes a very broad shoulder. The blue shift of the band indicates the increasing stabilization of the ruthenium *d*-orbitals by back bonding from ruthenium to the cyanide group. Such shifting is also observed in the complexes having ruthenium-bipyridine sub-unit as discussed earlier, and is in very good agreement with the shifting of ν(CN) to lower energy in the IR spectra. The shoulder at 261 nm in complex (2) and an absorption peak at 268 nm in complex (3), which are assigned to the MLCT transitions for the copper sub-units, are almost unaffected in their corresponding complexes (8) and (10), respectively, on bridge formation. The IL bands, in the higher energy regions, which are mainly localized on phenyl group, in the complexes (2) and (3) are mixed with the strong IL bands at 240 nm due to the complex $[(\eta^5\text{–Cp})Ru(PPh_3)_2Cl]$, in the bridged complexes, Figure 6.11. On bridge formation the

MLCT transition at 260 nm in complex (1) becomes broad and appears as a shoulder, whereas the MLCT transition band of the complex $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ shifts towards the higher energy region and becomes broad due to the reasons discussed earlier.

6.4 SUMMARY

New complexes of the formulae $[(N\text{-}N)Cu(PPh_3)CN]$ (N-N = 2,2'-bipyridine, 1,10-phenanthroline) have been isolated and used to synthesize novel cyano-bridged copper(I)-ruthenium(II) complexes $[(N\text{-}N)Cu(PPh_3)(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$ (bpy = 2,2'-bipyridine) and $[(N\text{-}N)Cu(PPh_3)(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$ (Cp = cyclopentadienyl anion). In addition, complexes $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(bpy)_2Cl]PF_6$ and $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(\eta^5\text{-}Cp)(PPh_3)_2]PF_6$ or BF_4 have been synthesized using $[(PPh_3)_2CuCN]$. All the complexes have been characterized on the basis of elemental analyses, spectroscopic data (IR, UV-vis, ^1H, ^{13}C and ^{31}P NMR), magnetic and conductivity measurements. Spectroscopic data clearly indicate that in these complexes cyanide is bridged between copper(I) and ruthenium(II) metal centres, and there is excessive π-back bonding from these metal centres to bridged cyanide group which results in significant decrease of $\nu(CN)$.

CHAPTER 7

CONCLUSIONS AND PROSPECTS

7.1 CONCLUSIONS

The studies embodied in the thesis are centred on copper(I) and ruthenium(II) π-acid complexes. Interaction of some of the thione ligands in presence of triphenylphosphine or triphenylarsine ligand has been studied in detail. Moreover, the studies on Cu(I)——CN——Ru(II) system has been carried out to examine the effect on ν(CN) when the cyanide group is bridging between the two electron-rich centres.

The conclusions drawn on the basis of these studies can be enumerated as follows.

1. Thione ligands react with $[Cu(EPh_3)_3X]$ (E = P, As; X = Cl, Br, I) to produce substituted products $[Cu(EPh_3)_2(LH)X]$ (LH = thione ligand).
2. These complexes adopt the distorted tetrahedral geometry.
3. The ligands are bonded to copper(I) through thione

sulphur and act as monodentate.

4. In all cases there is an intramolecular N——H·········X hydrogen bond.
5. The complex $[Cu(PPh_3)_2CN]$ reacts with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) to produce tetracoordinate compounds $[(N—N)Cu(PPh_3)CN]$ (N——N = bpy, phen) with the elimination of one triphenylphosphine.
6. Copper(I) complexes having Cu(I)——CN unit can be used to synthesize cyano-bridged complexes.
7. In the complexes having Cu(I)——CN——Ru(II) unit, there is excess π-back bonding from copper(I) and ruthenium(II) centres, resulting in decrease of ν(CN).

7.2 PROSPECTS

Although study of the complexes covering their synthesis, characterization and spectral aspects has been carried out, yet a large number of ramifications originate from such a study. A few of them are listed below:

1. Tetrameric and hexameric complexes of copper(I) with the deprotonated thione ligands have shown remarkable photoluminescence properties. On the same lines, the deprotonated thiones described in the thesis can be

used to prepare such polynuclear copper(I) complexes which may show desirable photophysical properties.

2. Work can be extended to stibine and the bismuthine analogues of the complexes.

3. By choosing the solvent and reaction conditions, pH of the reaction medium can be adjusted to force the deprotonation of the ligands described in the thesis. These monoanions (L^-) may function as bidentate chelating ligands. Possibly these anionic ligands will give $[Cu(EPh_3)_2L]$ and $[(L—L)CuL]$ on reaction with $[Cu(EPh_3)_3X]$ and $[(L—L)Cu(EPh_3)X]$ respectively. This type of bidentate chelating behaviour of these anions is worth exploring.

4. Reactions of $[Cu(EPh_3)_3X]$ with the tetradentate polypyridines namely 2,3-bis(2-pyridyl)-pyrazine (2,3-dpp), 2,5-bis(2-pyridyl)-pyrazine (2,5-dpp), 2,3-bis(2-pyridyl)-quinoxaline (2,3-dpq) and 2,2'-bipyrimidine (bpm), may give mononuclear complexes of the type $[(polypyridine)Cu(EPh_3)X]$ and/or the dinuclear complexes of the type $[X(EPh_3)Cu(polypyridine)Cu(EPh_3)X]$. In the later case polypyridine acts as tetradentate bridging ligand between two metal centres whereas, in the former case it acts as bidentate ligand. The reactions of

mononuclear complexes thus obtained can be carried out with the other metal centre unit *e.g.* $[Ru(bpy)_2Cl_2]$ in an attempt to prepare the heteronuclear bimetallic complexes. Moreover, reactions between these complexes and the deprotonated thione ligands (monoanionic) may yield complexes of the types [(polypyridine)Cu(L)] and/or [(L)Cu(polypyridine)Cu(L)] etc, where deprotonated ligands (L^-) are behaving as bidentate chelating ligands. In place of L^-, dithiolate ligands, e.g. maleonitriledithiolate (mnt^{2-}), 2,2-dicyano-1,1-ethylenedithiolate ($i\text{-}mnt^{2-}$) and N-cyanodithio-cabimate (cdc^{2-}), can also be used as terminal ligands. The above schemes for synthesis are based on the strategies of "Complexes as Metals and Complexes as Ligands". It will be revealing to attempt the above mentioned reactions.

5. The arsine, stibine and bismuthine analogues of the cyano-bridged complexes described in the thesis can be prepared to correlate the effects of these variations on the stretching frequency of the bridged cyano group and the electronic properties of the complexes.
6. The syntheses, reactivity and the characterization of

the following may be attempted. (a) Cyano-bridged copper(I) homometallic binuclear complexes of the type $[(L{-}L)(EPh_3)Cu(\mu\text{-}CN)Cu(EPh_3)(L{-}L)]^+$ (E = P, As, Sb, Bi). (b) The complexes of the type $[NC(L{-}L)_2Ru(\mu\text{-}CN)Cu(EPh_3)(L{-}L)]^+$ and $[(L{-}L)(EPh_3)\text{-}Cu(\mu\text{-}NC)(L{-}L)_2Ru(\mu\text{-}CN)Cu(EPh_3)(L{-}L)]^{2+}$. (c) The complexes of the type $[(\eta^5\text{-}Cp)Ru(EPh_3)_2(\mu\text{-}CN)Cu\text{-}(EPh_3)(L{-}L)]^+$.

7. Reactions of thione ligands with $[Cu(PPh_3)_2CN]$ can be attempted to prepare the pseudohalide analogues of the copper(I) complexes reported in the thesis. The compounds thus obtained can be utilized to prepare the cyano-bridged complexes.
8. The cyanide and/or polypyridine bridged homo- and heterometallic polynuclear complexes may show photophysical intercomponent properties, *e.g.* electron and energy transfer. Such studies may help in designing the suitable molecular devices of practical importance *e.g.* harvesting of solar energy for useful purposes. It will be worthwhile to carry out photophysical and electrochemical studies of these systems.

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